

CHARACTERIZATION AND CATALYTIC ACTIVITY OF DISPERSED  
TRANSITION METAL OXIDE PARTICLES ON CARBON SUBSTRATES

By

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Abstract of Dissertation Presented to the Graduate School  
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Requirements for the Degree of Doctor of Philosophy

CHARACTERIZATION AND CATALYTIC ACTIVITY OF DISPERSED  
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After modification of a CNDO2/U algorithm, a valence band density of states curve (VB DOS) is constructed from the resulting eigenvectors and eigenvalues for a distribution of MnO dimer structures. The resulting curve shows a remarkable similarity to the X-ray photoelectron spectroscopy (XPS) spectrum of a thick continuous film of MnO.

In order to investigate the properties of small particles using XPS, they must be isolated on supports. Different methods of preparing dispersed oxides on carbon foil supports are investigated. In particular, vapor and solution deposition are used to fabricate various transition metal oxides on carbon foil. Vapor deposition is used to disperse MnO and Mn<sub>2</sub>O<sub>3</sub> on the carbon substrate and solution deposition is used to disperse MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> on the substrate. Data

acquired by XPS from the samples of both methods indicate that two completely different surfaces result. Vapor deposition yields a surface in which the particles are confined to the surface. Solution deposition yields a surface whereby the particles have been incorporated into the surface. The electronic structure of these particles are investigated using valence band photoemission.

When the dispersed Mn oxides on carbon foil are placed in permanganate solution, it is found that the dispersed MnO has a greater effect on the autocatalytic decomposition of permanganate than does dispersed Mn<sub>2</sub>O<sub>3</sub>. It is also found that dispersed Mn<sub>2</sub>O<sub>3</sub> has a greater effect on this reaction than either the bulk or continuous film of the Mn(III) oxide. Dispersed MnO<sub>2</sub> on carbon foil are judged to have too high an effect on the reaction, possibly because of the particles which are incorporated into the surface.

## CHAPTER 1 INTRODUCTION

### Fundamental Principles of X-Ray Photoelectron Spectroscopy

The analytical methodology of X-Ray Photoelectron Spectroscopy (XPS) is an effective means for the chemical analysis of surfaces. In XPS, a solid is bombarded with X-Ray radiation, typically of energies of either 1487 or 1254 eV. Photoemission of electrons from the surface region of the solid occurs. The ejected photoelectrons are dispersed according to their kinetic energy (if an electrostatic analyzer is used) and then counted. The intensity of the signal is a function of the number of counts at a given kinetic energy. Conservation of energy requires that

$$h\nu = \text{B.E.} + \text{K.E.} + \phi_{\text{spect}}, \quad (1)$$

where  $h\nu$  is the energy of the incident X-Ray radiation, B.E. is the binding energy and K.E. is the kinetic energy of the photoelectron and  $\phi_{\text{spect}}$  is the spectrometer work function. The value of  $\phi_{\text{spect}}$  will vary from instrument to instrument, thus each instrument must be calibrated for this quantity. From the measured kinetic energy of the photoelectron its binding energy can be calculated by

$$\text{B.E.} = h\nu - \text{K.E.} - \phi_{\text{spect}}. \quad (2)$$

From the binding energies of photoelectrons, chemical information can be deduced about the surface.

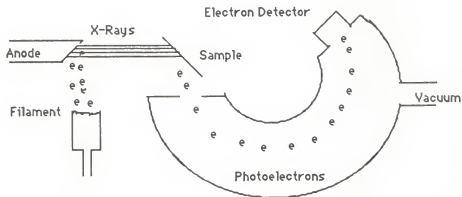


Figure 1-1. Schematic Representing Basic XPS Principles.

X-Ray bombardment of a surface can produce another type of electron other than a photoelectron. Upon the photoemission of an electron, a vacancy will develop after ejection. An electron with lower binding energy from another subshell can move in and fill the vacancy. This movement results in the dissipation of energy which can cause a third electron, known as an Auger electron, to be ejected. Auger electrons are denoted by three upper case letters. The first letter represents the subshell containing the electron which is ionized by the incident X-Ray radiation, the second represents the subshell containing the electron which fills the vacancy, and the third the subshell from which the Auger electron is ejected. The signal intensity or peak height is affected by parameters which do not affect the binding energies. One such parameter is the differential cross section for photoionization [1], which is given by

$$d\sigma(\epsilon)/d\Omega = \sigma_T(\epsilon)/4 [1 + \beta P_2(\cos(\theta))]. \quad (3)$$

It is seen that the intensity is a function of the total cross section for photoionization, which is the probability of observing an electron of a given energy for ionization, and the angle  $\theta$  between the incident photon beam and the direction of ejection of the photoelectron. The  $\beta$  term is known as the asymmetry parameter and is a term which is characteristic of a given molecular orbital. The value of  $\beta$  indicates what the preferred direction of the photoelectrons will be with respect to the incident photon beam. If  $\beta=+2$  as is the case for a spherically symmetric distribution of charge (an atomic  $s$  orbital), then the photoelectrons will be preferentially ejected at angles of  $90^\circ$  to the photon beam [1]. For orbitals having angular momentum (i.e.  $p$ ,  $d$  or  $f$ ),  $\beta$  values will be less than  $+2$ , which will cause the photoelectron to be preferentially ejected at different angles. If the intensity is plotted against  $\theta$  for many different values of  $\beta$  it is found that there is a "magic angle" of  $54.7^\circ$  where the intensity is independent of  $\theta$ . When spectrometers are operated at this magic angle, total cross sections can be used directly in quantitative analysis.

### Instrumentation

#### General Principles

An X-ray photoelectron spectrometer is composed of a x-ray source, a sample analysis chamber (SAC), an electron or energy analyzer, and a detector system, which is usually interfaced with a computer. X-rays are generated by bombarding a material (target)

with high energy electrons. When these electrons impinge upon the target they knock out its electrons, which creates vacancies. The photons are generated as a result of the higher energy electrons of the target filling the vacancies created by the ejection of the lower energy electrons. This process creates photons of various energies which then pass through either a Be or an Al window. This acts to partially filter the bremsstrahlung or x-ray continuum from the desired  $K_{\alpha}$  rays. Even after filtration, however, only about 50% of the photons are of the desired energy. The contribution to the photoelectron spectrum by the bremsstrahlung is not important because it is distributed over 2 KeV while the  $K_{\alpha}$  rays are concentrated in a peak of 1eV FWHM [1]. In addition to the  $K_{\alpha} 1,2$  line, other lines are present due to the difference in energy between the  $L_{II}$  and  $L_{III}$  levels. This difference is important because  $K_{\alpha} 3,4$  gives satellites in the spectra. With monochromatization it is possible to reduce the width of Al  $K_{\alpha} 1,2$  radiation to as little as 0.2 eV [2]. X-ray radiation can be monochromatized by allowing it to impinge upon a crystal which will cause it to be dispersed. After dispersion, radiation of a particular energy can be selected by means of a slit. This method is known as slit filtering. Another method involves the matching the dispersion of the crystal with that of the spectrometer. In this technique the X-rays are dispersed by the crystal before they reach the sample. Their dispersion will cause the resulting photoelectrons to come out at slightly different energies, depending on their position along the target. This dispersion is compensated for by the spectrometer so all electrons will be ejected as if they came from atomic orbitals having the

same energy [1]. Still another means to reduce the inherent line width of the radiation is the fine focusing method, which uses a rotating anode to concentrate the beam before it impinges upon the crystal. Its advantages are that it gives more photons after emergence from the monochromator and does not put any restrictions on the sample. Monochromatization removes those lines responsible for source satellites in the spectra.

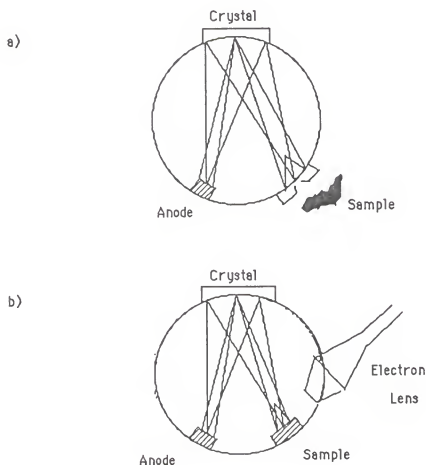


Figure 1-2. Schematics showing different types of monochromatization.

- a) Slit Filtering
- b) Dispersion Compensation

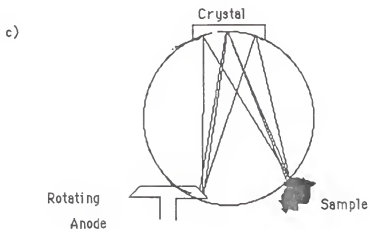


Figure 1-2.--continued

c) Schematic showing the fine focusing method of monochromatization.

It also removes all of the high energy brehmsstrahlung radiation, which is responsible for the decomposition of organic samples and some inorganic salts. The one disadvantage is that there is a large intensity loss for those instruments which employ a large sample area like the retarding grid instruments [2]. Figure 1-2 illustrates the above methods of monochromatization.

To avoid collisions between the X-rays and photoelectrons with the surrounding gas molecules, it is necessary to contain the source and sample in a high vacuum sample analysis chamber (SAC). In our instrument typically pressures as low as  $10^{-9}$  torr are achieved. With some degree of effort, namely by placing liquid nitrogen in the cold trap of the SAC, pressures as low as  $5 \times 10^{-11}$  torr are possible. The next major component of an X-Ray Photoelectron Spectrometer is the electron or energy analyzer. Photoelectrons are generated with a very broad spectrum of energies. Before an electron

with a particular kinetic energy can be counted by the detector system it must be separated from photoelectrons which have kinetic energies different from itself. The function of the electron analyzer is to perform this separation. The spectrum of photoelectron kinetic energies relative to the sample is not identical to the spectrum of photoelectron kinetic energies relative to the electron analyzer, because the sample and the spectrometer share a common ground, as seen by Figure 1-3. However, they are in one-to-one correspondence, since they differ by a constant factor, as shown by the following equations:

$$E_{kin} = E'_{kin} + (\phi_{sam} - \phi_{spect})$$

$$h\nu = E_{bin}^F + E'_{kin} + \phi_{sam}$$

$$h\nu = E_{bin}^F + E_{kin} + \phi_{spect}.$$

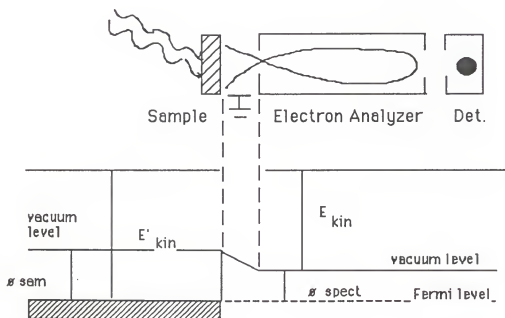


Figure 1-3. Diagram showing principles for the calculation of binding energies.

$E_{\text{bin}}^F$  is the Fermi level referenced binding energy of the electron in the sample. Thus, binding energies will be measured correctly only when the Fermi level of the sample is pinned to the Fermi level of the spectrometer. This is not possible for insulators, and the problem is further aggravated by sample charging which results from the photoemission process. The work function of the spectrometer is determined by calibrating it with a known standard, for example, the binding energy of the  $\text{Au}4f$  electron, which has a literature value of 83.8 eV. Auxiliary referencing must be employed for insulators. Most common are the gold decoration technique or referencing to the  $\text{C}_{1s}$  contamination peak.

There are three main types of analyzers which perform these functions. The two most important are the retarding grid and dispersion types. The retarding grid analyzer forces the electron to traverse a potential difference between two grids. This analyzer has a poor resolution and is not employed in any commercial x-ray photoelectron spectrometer. The dispersive type analyzer, which is most commonly used today, separates photoelectrons either according to their momentum or energy by making them traverse either a magnetic or electrostatic field respectively. The earliest dispersion analyzers were of the magnetic type. In this type analyzer, the photoelectrons are sorted according to their momentum. The equation which relates the magnetic field, with the path and momentum of the photoelectron is given by

$$B(\rho_0) = mv/ep_0. \quad (4)$$

The magnetic field is  $B$ ,  $m$  and  $v$  are the mass and velocity of the electron and  $\rho_0$  is the radius of the orbit of the electron. Double focusing can be understood by looking at Figure 1-4. If the photoelectron enters the analyzer at an angle  $\sigma$  to  $\rho_0$  (the optic circle), in the  $xy$  plane or at an angle  $\mu$  with respect to the  $z$ -axis, then it will return to the optic circle after it has traversed an angle of  $\pi\sqrt{2}$  or 255 degrees. In other words, the analyzer has the ability to redirect the deviation of the photoelectron whether it deviates in or out of the plane of  $\rho_0$ . The major advantage of the magnetic dispersion analyzers is that a greater field can be supplied for the study of high energy ( $>5000\text{eV}$ ) photoelectrons. At this energy relativistic effects become significant and the optics needed to study such electrons are better understood for magnetic instruments[1].

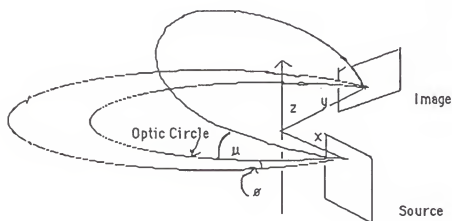


Figure 1-4. Principle of Magnetic Double Focusing Electron Analyzer.

One disadvantage of this type analyzer is that of cost. A magnetic analyzer comparable to an electrostatic one would cost approximately ten times as much. Another disadvantage of the magnetic analyzer instruments is their sensitivity to stray magnetic fields. If a resolution of 0.01% is desired the stray field must be reduced to 0.1 mG over a very large volume. To achieve this reduction of stray magnetism, very large compensating coils must be used. This makes the instrument as a whole very space consuming. Also, the stray fields must be monitored continuously [2].

Besides magnetic dispersive analyzers, there are also electrostatic type analyzers, which are more commonly used today because they cost less to construct and are less cumbersome. Their principle disadvantage is that they are unsuitable for studies involving high energy photoelectrons. If one is analyzing electrons with an eV greater than 2000, relativistic effects become noticeable. The optics for dealing with these effects are better understood for magnetic than for electrostatic analyzers. In an electrostatic analyzer, the photoelectron is dispersed according to its kinetic energy along a predescribed path. This is done by forcing the photoelectron to traverse an electrostatic field instead of a magnetic one. Such a field is achieved by placing a potential between two plates. The geometry of these plates determines the type of electrostatic analyzer. Several of the possible geometries of the plates are hemispherical and cylindrical. In our instrument hemispherical plates are employed. If we look at Figure 1-5 we can see a schematic diagram of a hemispherical electron analyzer. Equation (5) shows the relationship between the voltage between the

plates, the kinetic energy of the photoelectron, and the radius of its orbit in the analyzer.

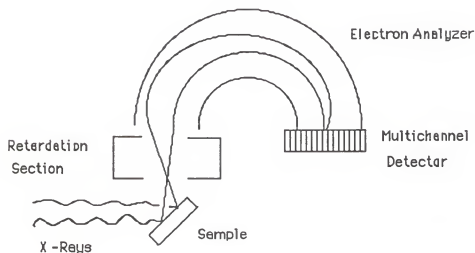


Figure 1-5. Schematic illustration of electron analyzer with retardation section.

$$V = E/e(R_2/R_1 - R_1/R_2) \quad (5)$$

This equation states that when a particular voltage is being applied between the plates, only photoelectrons of a particular kinetic energy will be able to completely traverse space between the plates and reach the detector. To measure the kinetic energies of all photoelectrons which are generated, the voltage is continuously varied over some specified range, usually with the aid of a computer which has been interfaced with the system. To reduce or lessen the tolerances of many of the mechanical components of the spectrometer, the photoelectron passes through a retardation section prior to its entry into the analyzer. If the kinetic energy of the electron is reduced from  $E_{\text{kin}}$  to some final  $E_0$ , the relative

resolution required from the analyzer is reduced from  $\Delta E_{kin}/E_{kin}$  to  $\Delta E_{kin}/E_0$ . If, for example, a spectrometer is required to achieve a resolution of 0.1eV for 1000eV electrons or 0.01% as the result of retardation, it would be required to achieve a resolution of 0.1eV for 100eV electrons. Retardation does reduce the intensity of the signal, however, so a trade-off between intensity and resolution results.

After the photoelectrons have been dispersed according to their kinetic energies, they must be detected and counted. Almost all detectors in XPS utilize continuous-dynode electron multipliers of the "channeltron" type [3-5]. These devices consist of glass tubes which have been doped with lead and then treated in such a way so as to leave the surface coated with a semiconducting material with a very high secondary electron emissive power [3]. A voltage of a few kV is placed between the ends of these tubes and electron multiplications of the order  $10^6$ - $10^8$  are achieved by repeated wall collisions as electrons travel down the inside of the tube [6]. As the voltage between the plates of the analyzer is swept, the electron counts at different kinetic energies is usually stored with the aid of a computer. Computer control is advantageous because it is desirable to make repeated scans over a spectral region to average out instrument drifts and to eliminate certain types of noise [6]. In many cases repeated scans are mandatory. Weak signals can result due to a small amount of the analyte or if the take-off angle (angle between the sample and the analyzer about which more will be covered in a later chapter) is at or near zero. The output from the electron multiplier can be linked directly to a plotter or printer for a single continuous sweep. The data system also allows one to

perform peak fits whereby spectral data can be resolved into Gaussian or Lorentzian distributions. For example the  $O_{1s}$  spectra can be resolved into a given number of these distributions which can then be compared to literature values. By doing so, various chemical species on the surface which contain oxygen can be deduced. Besides performing peak fits, it is possible to deconvolute XPS spectra so as to mathematically remove instrumental linewidth contributions. This term is not to be confused with peak fit.

### Instrument Employed

The instrument utilized for this work is the KRATOS XSAM 800. This instrument has a dual anode (either Mg or Al can be selected) x-ray source, a sample analysis chamber which can be pumped on by either a roughing, turbomolecular, ion, or titanium sublimation type pump, a hemispherical electron analyzer which includes a retardation section to reduce the kinetic energy of the photoelectrons before entering the analyzer, a detector consisting of an electron multiplier and a data system (A Digital Micro PDP-11 with 256 K bytes of RAM) to control the scanning of the photoelectrons and to collect and store the data. Peak fits are also possible at the convenience of the operator.

The X-ray source consists of a filament assembly which is essentially a tube with tungsten filaments which have been coated with thorium on either side. The thorium has a lower work function than the tungsten which makes the emission of electrons more efficient. The anode is a hollow metal rod with one end open so as

to allow cooling water to pass through and the other end capped with copper. The copper end resembles a roof with one side plated with Al and the other side with Mg. To generate x-rays, the emission stabilizer circuitry is first activated. This is a new circuit design by KRATOS which is supposed to generate a more stable emission of electrons from the filaments. After the emission stabilizer is activated, the high voltage power supply is switched on. Before this can occur, three safety interlocks must be satisfied. First, the pressure of the cooling water to the anode must be sufficient; second, the ion pump to the x-ray source must be on; and third, the ion gauge must be switched on. If these interlocks are satisfied, the power can be turned on. The desired voltage of the x-ray radiation is dialed up. Usually a value of 15kV is selected. The emission current is selected, and usually a value of 15mA is chosen. At this point the x-rays can be generated either by computer command or local command. When the Al anode is selected, the x-rays have an energy of 1487 eV, and when the Mg anode is chosen, the radiation is 1254 eV.

The sample analysis chamber (SAC) normally is kept at pressures between  $10^{-9}$  to  $10^{-11}$  torr. To achieve this extremely low pressure, it must be pumped in stages. First a roughing pump is used to evacuate the chamber to approximately 0.5 torr. After this pressure is obtained, a turbomolecular pump is used to bring the vacuum down to the  $10^{-3}$  torr region. The ion pump is switched on and in conjunction with the turbomolecular pump evacuates the chamber down to  $10^{-6}$  torr. The valve between the SAC and the turbomolecular pump is closed and the ion pump brings the vacuum

down to the operating range of  $10^{-9}$  torr. The specifications of the machine state that it is capable of reaching a pressure as low as  $5 \times 10^{-11}$  torr. To reach this pressure, however, it is necessary to add liquid nitrogen to the cold trap in the SAC. This procedure is very time consuming and is usually not necessary. To improve the efficiency of the ion pump, it may be used in conjunction with a titanium sublimation pump.

After the SAC has been pumped down to the  $10^{-9}$  torr range and the X-ray source has been activated, data can be acquired. This can be done with or without computer control. Almost always computer control is the option chosen. As stated previously the computer is a Digital Micro PDP-11 with the RT-11 operating system and 256K bytes of RAM. DS800, the software written by KRATOS, allows the user to acquire and process data off line. To acquire data, one simply chooses that option from the master menu which first appears after the system is booted. After the data acquisition menu appears one selects the region(s) which is (are) to be scanned, the number of sweeps to be performed in that region and the time allowed for each sweep. In addition, the operator has the choice of excitation source (either Al or Mg), low or high magnification, low or high resolution, and analyzer mode (either FRR or FAT). After the parameters have been selected, data acquisition can begin. One chooses the run option and assigns a file name to that run. The file name can be anything with six or fewer characters. One parameter that the computer cannot control on our instrument is the angle between the analyzer and the sample (sometimes referred to as the take off angle). This has to be adjusted manually. After the data has been collected and

stored, it can be viewed by choosing the off line processing option. After this option is chosen the data file name is typed in and the data appears in the form of spectra. The y-axis represents the intensity of the signal (number of photoelectron counts for a given kinetic energy) and the x-axis can represent either the binding or kinetic energy of the photoelectrons. It is also possible to perform depth profiling, which is done in conjunction with the ion gun. The ion gun creates argon ions which are directed as a beam to the sample. The beam strips away successive layers of the sample and the composition of each layer is determined. One of the disadvantages of this technique is that it destroys the sample. If one is using the sample in a catalytic experiment it might be preferable to use the sample after it has been analyzed. Also, matrix effect data is not attainable. Very rarely is the analyte going to be unaffected by the matrix in which it resides. Depth profiling works from the premise that all of the molecules are going to be sputtered at an equal rate, which is not the case. For example, in my work with dispersed manganese dioxide on carbon substrates, one factor which causes the molecules to be sputtered at different rates is the difference in the weights between the manganese and carbon atoms.

## CHAPTER 2 BACKGROUND OF THEORETICAL RESEARCH UNDERTAKEN

### Overview of Molecular Orbital Theory

#### Fundamental Principles

One aspect of the research that is undertaken here involves the effect of variation of the molecular geometry of clusters of the formula  $(\text{MnO})_2$  on the XPS valence band density of states (VBDOS). To show this effect, results of molecular orbital theory are compared with XPS valence band spectra. This comparison is possible as a result of the theory of Koopman [7-8], which states that the negative of an eigenvalue or molecular orbital energy ( $-\epsilon$ ) is equal to the binding energy (B.E.) of the photoelectron as given by

$$-\epsilon = \text{B.E.}$$

By making comparisons between eigenvalues and XPS valence band data, information can be deduced about the electronic structure of discontinuous clusters of deposited material on the surface of a substrate. Using the postulates of quantum mechanics, the eigenvalues can be obtained from the wavefunction of a system, as discussed briefly below.

The particle, detected by XPS, can be regarded as a wave, with the wavelength given by the de Broglie relation given by

$$mv = p = h/(\lambda)$$

$$\text{or } \lambda = h/p, \quad (6)$$

where  $p$  is the particle momentum and  $h$  is Planck's constant [6]. This wave behavior of the electron can be characterized by a wave function  $\Psi(r,t)$ , which contains all the information possible about it [9]. The Schrodinger equation, which allows eigenvalues to be extracted from the wavefunction, can be derived from the de Broglie relationship and the classical time-independent wave equation. It is given by

$$i\hbar/4\pi^2(\partial/\partial t) \Psi(r,t) = -(\hbar^2/8\pi^2m) \Delta \Psi(r,t) + V(r,t)\Psi(r,t), \quad (7)$$

where  $\Delta$  is the Laplacian operator  $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ . This equation describes the motion of a particle when it is under the influence of a potential  $V(r,t)$ . The Laplacian operator and the potential acting together on  $\Psi(r,t)$  form the Hamiltonian operator, which represents the total energy of the system. The wavefunction  $\Psi(r,t)$  must meet certain conditions, however, in order for the equation to be valid. These conditions derive from the postulate of quantum mechanics which states that a system of particles must be described by a square-integrable function. Thus  $\Psi(r,t) = \Psi(q_1, q_2, q_3, \dots, w_1, w_2, w_3, \dots, t)$ , where the  $q$ 's are the space coordinates, the  $w$ 's are the spin coordinates, and  $t$  is the time coordinate.  $\Psi^*\Psi$  is the probability that the space spin coordinates lie in the volume element

$d\tau (=d\tau_1, d\tau_2, \dots)$  at time  $t$ , if  $\Psi$  is normalized. To be acceptable the function must be single valued, nowhere infinite, continuous, with a piecewise continuous first derivative [8], as seen in Figure 2-1.

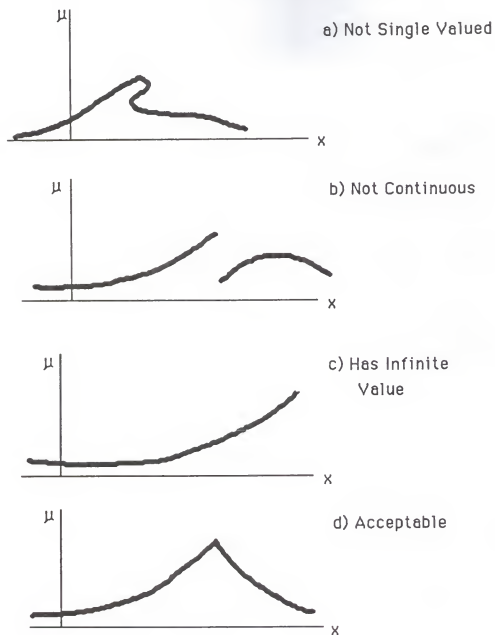


Figure 2-1. Illustrations of unacceptable and acceptable wavefunctions.

The more familiar form of the Schrodinger equation (7) is

$$H\Psi = E\Psi, \quad (8)$$

where  $H$  is the Hamiltonian operator and  $E$  is the energy. Equation (8) is an example of a class of equations called eigenvalue equations as shown by

$$Opf = cf, \quad (9)$$

where  $Op$  is an operator,  $f$  is a function called an eigenfunction and  $c$  is a constant called an eigenvalue. Therefore  $\Psi$  is an eigenfunction. In equation (7)  $V$  is the potential energy, and the second derivatives of the wavefunction  $\Psi$  are related to the kinetic energy. This is so because the second derivative of  $\Psi$  with respect to a given direction of measure is the rate of change of slope (i.e. the curvature) of  $\Psi$  in that direction. A wave function with more curvature will yield a greater kinetic energy. This is in agreement with the de Broglie relationship which states that a wave with a shorter wavelength will have a greater kinetic energy. Since we have a constant  $E$ , the wave must have more curvature in regions where the potential energy is low and visa versa [8]. The wavefunctions which are associated with a particle are related to its momentum by equation (6). In addition, the wavefunctions are eigenfunctions of the Schrodinger equation (8) and must meet the conditions which are illustrated in Figure 2-2. Also, the absolute square of the wavefunctions (i.e.  $|\Psi|^2$ ) is proportional to the probability density for finding a particle. If  $\Psi$  is an eigenfunction of equation (8), then  $k\Psi$  is also an eigenfunction, where  $k$  is a constant. Since  $k$  can be any

number, a problem arises as to which value  $k$  should be. Since the absolute square  $|\Psi|^2$  is proportional to the probability density for finding an electron,

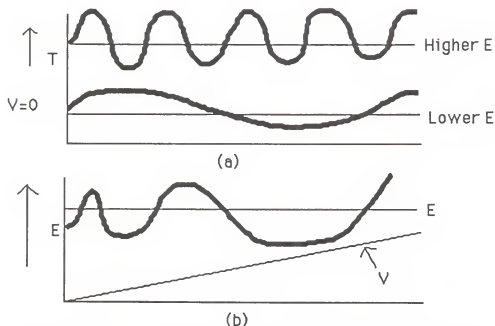


Figure 2-2. Illustration showing relationship between wave curvature and energy.  
 (a) When the potential energy  $V=0$ , the higher energy has more curvature (more wiggly). (b) As  $V$  increases the wavefunction becomes less wiggly [8].

then the probability of finding a particle between  $x=-\infty$  and  $x=\infty$  must be 1. The following equation is given by

$$k^*k \int \Psi^*(x)\Psi(x)dx = 1. \quad (10)$$

If selection of the  $k$  multiplier is made such that (10) is satisfied, then the wave function  $\Psi' = k\Psi$  is normalized. If two different

eigenfunctions  $\Psi_a, \Psi_b$  are integrated over  $x$ , they must give zero as a result, as shown by equation (11)

$$\int \Psi_a \Psi_b dx = 0. \quad a \neq b \quad (11)$$

Such wavefunctions are orthogonal. If wavefunctions are normalized and orthogonal, they are said to be orthonormal.

A second postulate states that when a dynamical variable of an operator is measured, that the measurement is one of the eigenvalues of that operator. If a large number of identical systems have the same function  $\Psi$ , then the average number of measurements on the variable  $M$  is given by

$$M_{av} = \int \Psi^* M \Psi d\tau. \quad (\text{if } \Psi \text{ is normalized}) \quad (12)$$

By linking the postulates together, and knowing the Hamiltonian operator represents the total energy of the system, the average value for the energy of a large number of identical systems can be obtained. This is given by equations (13) and (13a).

$$E = \int \Psi^* H \Psi d\tau \quad (\text{if } \Psi \text{ is normalized}) \quad (13)$$

The bra-ket form of (13) is

$$E = \langle \Psi | H | \Psi \rangle. \quad (13a)$$

In molecular orbital calculations, the energy of the system is minimized according to equation (13). Before this can be done however, it is necessary to formulate the Hamiltonian operator for the system and the form of the wavefunction  $\Psi$ . To formulate the

Hamiltonian operator, one must account for the total energy of the system. Terms must be formulated for the kinetic energy of the electrons, the potential between the electron and the nucleus and the electrostatic repulsion between electrons. Formulation of these terms results in an equation given by

$$H = -(1/2) \sum_{i=1}^n \Delta_i^2 - \sum_{\mu=1}^N \sum_{i=1}^n (Z_{\mu}/r_{\mu i}) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n 1/r_{ij}. \quad (14)$$

The letters  $i$  and  $j$  are indices for the  $n$  electrons and  $\mu$  is an index for the  $N$  nuclei. In principle wavefunctions can be symmetric or antisymmetric. An antisymmetric wavefunction has equal amounts of area represented by (+) and (-) regions. Symmetric wavefunctions do not. This principle can be seen in Figure 2-3.

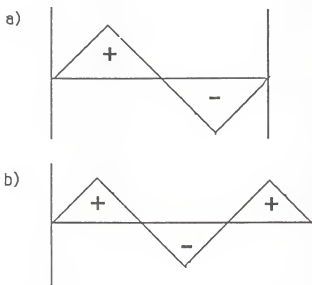


Figure 2-3. Figure showing principle of antisymmetric and symmetric wavefunctions.  
a) antisymmetric; b) symmetric

The Heisenberg uncertainty principle states that the ability to "see" electrons in an atom would perturb it so strongly that it could not be

assumed to be in the same state after measurement. Therefore there is no way of distinguishing electron (1) at position  $r_1$ , from electron (2) at position  $r_2$ . If we want to know  $r$ , we can only average together  $r_1$  and  $r_2$ . Since we cannot distinguish electron (1) from electron (2), the wavefunction  $\Psi$  can not be written as simply the product of one electron functions  $\phi$  of the form

$$\Psi = \phi_1(1)\phi_2(2)\phi_3(3) \dots \quad (15)$$

Since electrons are fermions, which are particles with half integral spin, the wavefunctions are required to be antisymmetric with respect to electron exchange. This behavior is accounted for if the wavefunctions are written in the form of a Slater determinant [6]. For example, for a two electron system, the wavefunction would be given by the following equation:

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix}$$

The general form for the Slater determinant is

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\phi_2(1) \dots \phi_n(1) \\ \phi_1(2)\phi_2(2) \dots \phi_n(2) \\ \vdots \\ \phi_1(n)\phi_2(n) \dots \phi_n(n) \end{vmatrix}$$

In molecular quantum mechanics it is very important to calculate eigenvectors and eigenvalues which represent electrons moving in a

"self consistent field" or SCF. The reason for this importance is seen by looking at the last term in the equation for the Hamiltonian operator (14), which is the interelectronic repulsion operator. Because electrons repel each other, the electron density is more diffuse than it would otherwise be. Electron (2) "sees" electron (1) as a smeared out, time averaged cloud. Electron (2) "sees" electron (1) as a smeared out, time averaged cloud. Electron (2) is thus screening the positive nucleus from electron (1). Since the nucleus is being screened, electron (1) will occupy a less constricted orbital than it otherwise would. If electron (1) is in a 1s orbital, its orbital as a result of this screening is represented by

$$1s'(1) = \sqrt{\zeta'^3/\pi} \exp(-\zeta' r_1). \quad (\text{electron (1)}) \quad (16)$$

A numerical value for  $\zeta$ , which is related to the screened nuclear charge seen by electron (1), can be determined. Likewise electron (2) is being screened by electron (1) in its expanded orbital  $\zeta$ . A value for  $\zeta'$  can therefore be determined for electron (2).  $\zeta'$  will be different from  $\zeta$  because the shielding of the nucleus by electron (1) is different from the previous step. Each change in  $\zeta$  for electron (1) necessitates a change in  $\zeta'$ . This process is continued until the two values (i.e.  $\zeta$  and  $\zeta'$ ) converge. When this happens electrons (1) and (2) are being screened by the same amount. The potential due to the nucleus and charge cloud of each electron causes the orbital for each electron to be self consistent. The electrons move in a self consistent field [8].

The one electron wavefunction  $\phi_i$  for a molecular orbital must be expressed in some mathematical form. The manner in which this is done is to express it as a linear combination of atomic orbitals (LCAO). If  $\phi_i$  is the molecular orbital it can be expressed by

$$\phi_i = \sum c_{ji} \chi_j, \quad (17)$$

where the  $\chi_j$ 's are the atomic orbitals and the  $c_{ji}$ 's are the coefficients. The coefficients of the atomic orbitals are known as an eigenvector. The atomic orbitals  $\chi_{ji}$  can be written as a function of the following variables:

$$\chi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi). \quad (18)$$

The variables  $r$ ,  $\theta$ , and  $\phi$  are expressed in terms of spherical polar coordinates as illustrated by Figure 2-4. The  $Y_{lm}(\theta, \phi)$  part has angular dependence and is explained by spherical harmonics.

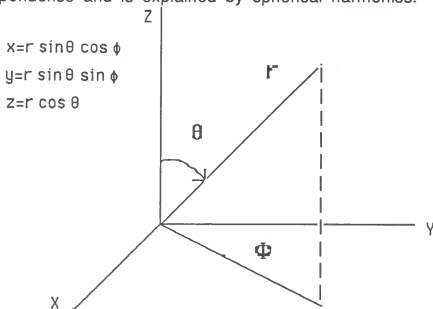


Figure 2-4. The relationship between spherical polar  $(r, \theta, \phi)$  and cartesian coordinates  $(x, y, z)$ .

It can further be broken down as exemplified by the equation given by

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi). \quad (19)$$

To be sure that the wavefunction will be unchanged if  $\theta$  or  $\phi$  is replaced by  $(\theta+2\pi)$  or  $(\phi+2\pi)$  the spherical harmonics depend upon the angular-momentum quantum numbers  $l$  and  $m$ , which arise in the solution of differential equations involving angular coordinates  $\theta$  and  $\phi$ . The radial part of the atomic orbital  $R_{nl}(r)$  is a function of exponential decay function (exp) and can take either the Slater-type [10] form

$$r^{n-1} \exp(-\zeta r) \quad (20)$$

or the Gaussian type form

$$r^{n-1} \exp(-\zeta r^2). \quad (21)$$

The Slater type orbital is used in the research undertaken in this dissertation. Slater functions behave better in the region of  $r=0$  and do not fall off as sharply as do the Gaussian type orbitals [11].

The orbital exponent  $\zeta$  is a function of how "spread out" the orbital is. The formula for  $\zeta$  is given by

$$\zeta = (Z-s)/n^*, \text{ where } n^* \text{ is the effective principal number,}$$

$s$  is the screening constant and  $Z$  is the atomic number. The greater the screening by the other electrons, the smaller will be the value of  $\zeta$  and the more diffuse the orbital will be. The effect of the value of  $\zeta$  on the orbital is shown by Figure 2-5.

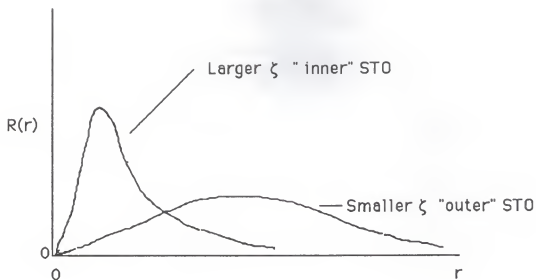


Figure 2-5. Schematic showing the effect of the Slater exponent on the radial portion of an atomic orbital.

### Self-Consistent Field Theory

As was mentioned in the previous section, it is necessary to determine eigenvalues and eigenvectors which are the result of electrons moving in a self-consistent field. From equation (13), the energy is obtained by allowing the Hamiltonian operator  $H$  to operate on the probability density  $\Psi^*\Psi$ .  $H$  can be broken down into a one electron part  $H_1$  and a two electron part  $H_2$  as illustrated by

$$H = H_1 + H_2. \quad (22)$$

The one electron part is a function of the kinetic energy of the  $i$ th electron and the potential between that electron and the nucleus. If summed over all electrons we have

$$H_1 = \sum_p H_{\text{core}}(p), \quad (23)$$

where 
$$H_{\text{core}}(p) = (-1/2) \Delta p^2 - \sum_A Z_A r_p A^{-1}. \quad (24)$$

The two electron part of equation (22) is  $H_2 = \sum_{p < q} r_{pq}^{-1}$ . (25)

Equation (13a) is given by

$$E = \langle \Psi | H | \Psi \rangle,$$

where 
$$E = \langle \Psi | H_1 | \Psi \rangle + \langle \Psi | H_2 | \Psi \rangle. \quad (26)$$

The wavefunction  $\Psi$  must be written as a Slater determinant so that electron exchange can be incorporated into it. Allowing a permutation operator  $P$  to act on the wavefunction is the equivalent to writing the wavefunction as a Slater determinant. The expectation value of the one electron operator is

$$H_{ij} = \int \Psi_i(1)^* H_{\text{core}} \Psi_i(1) d\tau_1. \quad (27)$$

The two electron Hamiltonian is a function of the two electron operator  $1/r_{pq}$  (equation 25). This operator gives the electrostatic coulomb repulsion energy between two charge clouds [8]. A matrix element of this electrostatic coulomb repulsion is defined as

$$J_{ij} = \iint \Psi_i^*(1) \Psi_j^*(2) (1/r_{pq}) \Psi_k(1) \Psi_l(2) d\tau_1 d\tau_2. \quad (28)$$

The value of this integral represents the repulsion between electron (1) on orbitals  $\Psi_i$  and  $\Psi_k$  and electron (2) on orbital  $\Psi_j$  and  $\Psi_l$ . Since the charge clouds are everywhere negative, their product causes  $J$  to be everywhere positive. The entire matrix would represent the electrostatic repulsions between all orbitals in the molecule including differential overlap where  $\Psi_i^*(1) \Psi_k(1)$ . Another integral

that results from the evaluation of the two electron Hamiltonian is the exchange integral denoted by  $K$ . This integral gives the interaction between an electron "distribution" and another electron in the same distribution [8]. The exchange integral is given by

$$K_{ij} = \iint \Psi_i^*(1) \Psi_j^*(2) (1/r_{pq}) \Psi_j(1) \Psi_i(2) d\tau_1 d\tau_2. \quad (29)$$

By collecting terms the formula for the total electronic energy is given by

$$E = 2 \sum_i^n H_{ii} + \sum_i^n J_{ii} + \sum_i^n \sum_{j(\neq i)}^n (2J_{ij} - K_{ij}) \quad (30)$$

and the orbital energies are given by

$$\varepsilon = H_{ii} + \sum_j^n \{ 2J_{ij} - K_{ij} \}. \quad (31)$$

The derivation of the Fock operator is very complex and it is not necessary for it to be presented here. If interested in its derivation consult reference 8 appendix 7. By utilization of the previously mentioned terms, the Fock operator is given by

$$F = [ H_{core}^{(1)} + \sum_j (2J_j(1) - K_j(1)) ]. \quad (32)$$

which leads to the following equation in the eigenvector form.

$$F\phi_i = \varepsilon\phi_i \quad (33)$$

Self consistency is achieved by making an initial guess at the molecular orbitals  $\phi_i$ . These MOs are used to construct a Fock

operator, which is used to solve for the new MOs (i.e.  $\phi'$ ). These are then used to construct a new  $F'$  and so on until no significant change is detected. The solutions are said to be self-consistent.

### Approximations to Molecular Orbital Theory

#### Basic Principles of Complete Neglect of Differential Overlap (CNDO)

The SCF principles that were outlined above involve very lengthy algorithms (some methods have more than 80,000 lines of code) and as a result, require a considerable amount of computer memory and CPU time in order to execute. As a result, approximations have been applied to SCF principles. Thus considerably shorter codes (typically between 1200-1600 lines) requiring less computer memory are obtained. One of the best known examples of approximate molecular orbital theory is complete neglect of differential overlap (CNDO) written by John A. Pople and associates in 1965 [12-13]. Such an approximate method is also referred to as semiempirical because the eigenvectors and eigenvalues no longer result solely from the principles of quantum mechanics. Experimental data is used in the formulation of the Fock matrix.

The first approximation in CNDO which is applied to SCF theory applies to the formulation of the overlap integral matrix. This matrix is composed of values which show the degree of overlap between the various atomic orbitals in the molecule. The approximation consists of replacing the overlap matrix by a unit

matrix whereby all elements are zero except the diagonal elements which are 1. In the normalization of Roothaan's equations  $\sum (\mathbf{F}_{\mu\nu} - \epsilon \mathbf{S}_{\mu\nu}) \mathbf{C}_{\nu i} = 0$  [14]. By ignoring differential overlap,  $\mathbf{S}_{\mu\nu} = 0$  for  $\mu \neq \nu$ . In other words, the atomic orbitals are treated as if they were orthogonal and as a result, the Roothaan equations reduce to  $\sum \mathbf{F}_{\mu\nu} \mathbf{C}_{\nu i} = \epsilon_i \mathbf{C}_{\mu i}$  where  $\mathbf{F}_{\mu\nu}$  is the Fock operator,  $\mathbf{C}_{\nu i}$  is the eigenvector or coefficients to the same atomic orbital as the Fock operator and the  $\epsilon_i$ 's are the eigenvalues or molecular orbital energies. This approximation becomes more severe as the internuclear distance decreases, however, because it causes larger and larger electron populations to be ignored. The second approximation results in a simplification of equation (28), which computes the matrix elements of the electrostatic coulomb repulsion between charge clouds. The approximation neglects all differential overlaps in two electrons integrals. Differential overlap occurs when  $\Psi_i^*(1)\Psi_j(1) \neq 0$ , where probability density is coming from electron (1) over orbitals  $i$  and  $j$ . Such electron densities are exceedingly numerous and also exceedingly small. Ignoring differential overlap means that equation (28) vanishes unless  $i=k$  and  $j=l$ . This has the obvious benefit of reducing the number of integrals that need to be evaluated. The third approximation, which results from the second, is to reduce the number of coulomb repulsions to one value per atom pair. Differential overlap can be monoatomic, where  $\Psi_i\Psi_k$  is on the same atom or diatomic where  $\Psi_i\Psi_k$  is on different atoms. For the monoatomic case neglect of differential overlap causes invariance of rotation to be negated. This means that rotation of an atom with respect to another atom will

result in a different set of eigenvalues and eigenvectors. To restore invariance, there is an additional approximation made. The remaining two electrons integrals will not be dependent upon the nature of the atomic orbitals, but on the atoms to which  $\Psi_i$  and  $\Psi_k$  belong [11]. This can be shown as

$$(ii|kk) = \Gamma_{AB} \text{ for all } i \text{ on atom A and for all } k \text{ on atom B.}$$

$\Gamma_{AB}$  is the average electrostatic repulsion between any electron on atom A and any on atom B [11]. The value of  $\Gamma_{AB}$  is given by

$$\Gamma_{AB} = \iint s_A^2(1) (1/r_{12}) s_B^2(2) d\tau_1 d\tau_2. \quad (34)$$

As equation (34) shows all orbitals are taken to be of the "s" type. The fourth approximation is to neglect differential overlap in the interaction integrals involving the cores of other atoms where

$$(i|VB|k) = V_{AB} \text{ if } i=k. \text{ If } i \neq k \text{ the integral vanishes.}$$

$V_{AB}$  is the interaction between any electron on atom A with the core of atom B. Therefore, any differential overlap between two atomic orbitals on atom A will be ignored in the calculation of this interaction.

The last approximation made in CNDO is to allow off diagonal matrix elements in the Hamiltonian to be proportional to the overlap integrals. This is shown by

$$H_{ik} = \beta_{AB} S_{ik}, \quad (35)$$

where  $\beta_{AB}^0$  is the bonding parameter, which is characteristic of a particular atom. As the overlap increases, the bonding capacity of the overlap will increase [11]. With all these approximations, the Fock matrix elements can be computed and are given by

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - 1/2 P_{\mu\mu}) \Gamma_{AA} + \sum_{B(\neq A)} (P_{BB} \Gamma_{AB} - V_{AB}) \quad \text{and} \quad (36)$$

$$F_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} - 1/2 P_{\mu\nu} \Gamma_{AB}. \quad \mu \neq \nu \quad (37)$$

Equation (36) can be rearranged into

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - 1/2 P_{\mu\mu}) \Gamma_{AA} + \sum_{B(\neq A)} [-Q_B \Gamma_{AB} + (Z_B \Gamma_{AB} - V_{AB})] \quad (38)$$

and the total energy can then be derived. This is shown by

$$E_{\text{Total}} = (1/2) \sum_{\mu\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + \sum_{A < B} Z_A Z_B R_{AB}^{-1}. \quad (38a)$$

To achieve self-consistency an initial guess is made of the molecular orbital coefficients. The diagonal elements of the Fock matrix (i.e.  $F_{\mu\mu}$ ) come from experimental values for the ionization potentials (i.e.  $U_{\mu\mu}$  in equation (38)). The off diagonal elements (i.e.  $F_{\mu\nu}$ ) are replaced by  $\beta_{AB}^0 S_{\mu\nu}$ . The electrons are then assigned to M.O.s with the lowest energy (i.e. lowest eigenvalues). The density matrix, which is given by

$$P_{\mu\nu} = \sum_i^{\text{occ}} c_{\mu i} c_{\nu i}, \quad (39)$$

is calculated from the coefficients of the occupied atomic orbitals. This matrix is used to formulate a new Fock matrix  $F_{\mu\nu}$ . When the Fock matrix is diagonalized a new set of eigenvectors and

eigenvalues are produced. They are then used to reassign the electrons in pairs to the molecular orbitals with the lowest energy and to construct a new density matrix. These steps are repeated until self-consistency is achieved [11]. Figure 2-6 shows the effect of self consistency upon the radial part of a wavefunction. This program utilizes the modifications made in the second parameterization of CNDO. These modifications include the incorporation of the "zero penetration effect" which equates the last term in parenthesis in equation (38) to zero and the replacement of the ionization potentials in the  $U_{\mu\mu}$  term with the average of the ionization potential and the electron affinity (i.e.  $-1/2 (I_{\mu} + A_{\mu})$ ).

#### CNDO2/U

A relatively new CNDO algorithm was selected for this project. Unlike the version written by Pople et al., [12,13] this program is parameterized for the first 81 elements of the periodic table. This is possible by the utilization of the concept of "fictitious atoms," whereby those elements which have their valence electrons distributed over two or more subshells with different principal quantum numbers, are treated as two or more atoms which are centered at the same coordinate. Figure 2-7 illustrates this principle.

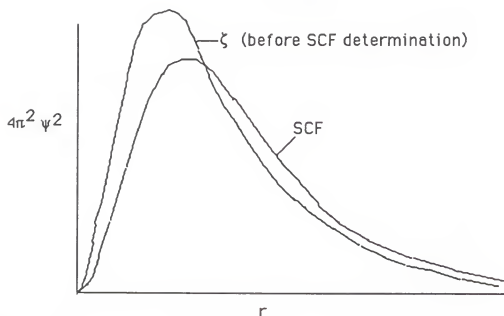
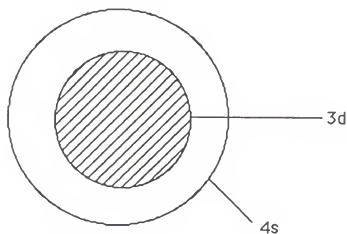


Figure 2-6. Effect of SCF calculation upon the electron distribution.

Although this program retains the concepts outlined in the previous section, one of the major differences between this program and the earlier version is in the formulation of the coulomb repulsion matrix.



First Row Transition Element

Figure 2-7. Illustration of how a first row transition element is treated in CNDO2/U.

From the last section it was stated that there is one matrix element calculated per atom pair. However for a first row transition element there are  $ns$  and  $(n-1)d$  valence electrons. It therefore would be necessary to calculate the following  $\Gamma$  values:

$$\Gamma (n-1)d (n-1)d ; \quad \Gamma (n-1)d ns ; \quad \Gamma ns ns.$$

In addition to this modification in the formulation of the coulomb integral matrix, there is also a modification in the calculation of the atomic energies of transition type elements. Since the transition element is considered to be two atoms it is necessary to calculate two atomic energies for each atom. The equation used is given by

$$AE = s \cdot ENEG(s) + p \cdot ENEG(p) + (TE^2 \cdot \Gamma(l,l)/2.) + d \cdot ENEG(d). \quad (40)$$

where  $AE$  equals the atomic energy,  $ENEG$  is the average of the ionization potential and the electron affinity for the respective subshell.  $TE$  equals the total number of electrons and  $s$ ,  $p$ , and  $d$  equal the number of  $s$ ,  $p$ , and  $d$  electrons, respectively.

# CHAPTER 3

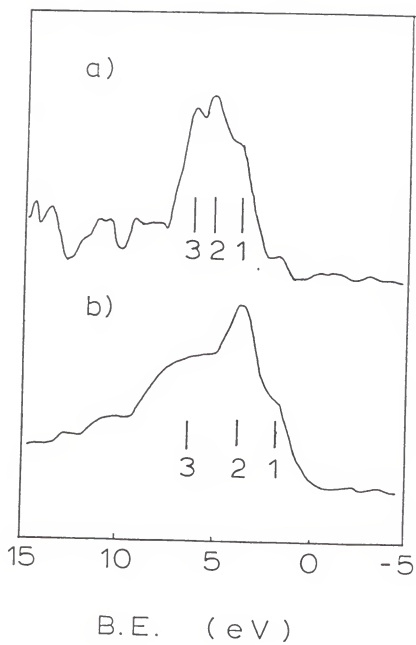
## THE EFFECT OF VARIATION OF MOLECULAR GEOMETRY OF A TRANSITION METAL OXIDE CLUSTER ON THE VALENCE BAND DENSITY OF STATES

### Background

Dispersed particles or clusters, which usually have catalytic properties on inert substrates such as carbon, silica, or aluminum oxide, have been the focus of much investigation [15-26]. Investigations have focused primarily on their electronic structure- experimentally, through the use of electron spectroscopy and theoretically, through various molecular orbital algorithms. The electronic structure of these deposited clusters can be investigated by observing the shifts in binding energy of the main photoelectron peaks in the relevant core regions and through acquisition of valence band spectra. It has been reported in a study on the electronic structure of catalytic metal clusters (i.e. Pd and Pt) that the valence band undergoes a narrowing and a shift away from the Fermi level relative to the bulk metal as the metal clusters become more highly dispersed [27]. Unlike dispersed metals on inert substrates, relatively little attention has been paid to the electronic structure of dispersed metal oxides on inert substrates. As a result, the electronic structure of dispersed and bulk like MnO on carbon foil has been performed by Zhao and Young [28]. It was determined that

Figure 3-1. Comparison of spectra of highly dispersed and continuous film of MnO on carbon foil.

- a) The valence band spectrum of highly dispersed MnO on carbon foil.
- b) The valence band spectrum of a thick continuous film of MnO on carbon foil.



for highly dispersed MnO on carbon foil (a coverage of 0.22) the valence band undergoes a narrowing and a shift in its binding energy away from the Fermi level relative to bulk material, as can be seen in Figure 3-1. In the case of supported metal particles, this behavior led to investigations which sought to correlate XPS valence band behavior with results from molecular orbital (M.O.) algorithms to determine the minimum or threshold number of atoms required for a cluster to exhibit properties of the bulk material. For example, R.C. Baetzold et al. performed an investigation into the determination of the particle size required for bulk metallic properties [29]. Extended Huckel calculations were performed on clusters with face-centered cubic (fcc) geometry of sizes ranging from 13 to 79 atoms. The results from the calculations were used to construct valence band density of state curves and the width of the d band was determined. For the largest cluster size (i.e. 79) it was determined that the d bandwidth was 86% of that for the bulk material and for a cluster of 13 atoms the d bandwidth was 50% of that of the bulk material. Table 3-1 shows the results.

Table 3-1  
Comparison of d bandwidths with cluster size

| cluster          | Pd <sub>2</sub> | Pd <sub>13</sub> | Pd <sub>31</sub> | Pd <sub>55</sub> | Pd <sub>79</sub> | Bulk Pd |
|------------------|-----------------|------------------|------------------|------------------|------------------|---------|
| d band-<br>width | 0.80            | 1.54             | 2.26             | 2.57             | 2.65             | 3.08    |

What is done can be summed up by the following statement. For  $(M)_X$ , where  $X=1,2,3,4 \dots$ , and where  $M$  is some monomer unit, as  $X$  is increased the electronic structure evolves to that of the bulk material. In Baetzold's study the selection of one geometry (i.e. fcc) for all cluster sizes is arbitrary. It seems reasonable that when a substance is deposited either fractionally or partially on a substrate that it will not form the same geometry for all possible values of  $X$ . The goal of this research project is to see what effect the variation of the molecular geometry for a given cluster size would have on the valence band density of states (VBDOS). Could a "bulk like" VBDOS curve be constructed by variation of the smallest possible cluster size for MnO, namely  $(MnO)_2$  ?

As was mentioned briefly at the beginning of chapter 2, the binding energy of the photoelectron is linked to eigenvalues derived from molecular orbital theory by the rule of Koopman [7-8], which can be represented by

$$-\epsilon \text{ (eigenvalue)} = \text{binding energy of the photoelectron.} \quad (41)$$

This rule is not entirely correct, however, because it is based on an incorrect assumption-that the orbitals remain frozen orbitals during photoemission. This is a "static" approximation. In actuality the remaining electrons "relax" towards the site of photoemission because of reduced screening of the nuclear charge. This relaxation imparts a certain amount of kinetic energy to the ejected electron, thus reducing its binding energy. If comparisons are being made between clusters of different size, where the extent of relaxation is

different, this limitation of Koopman's rule could be a problem. In addition, the rule of Koopman also neglects correlation energy, which is due to electron repulsion. Since we are interested in the relative eigenvalues for clusters where the number of atoms is held constant, this limitation should not be a problem.

### Modification of CNDO/2U Algorithm

In this work, the semiempirical molecular orbital method of CNDO/2U [30] is utilized to determine the eigenvectors and eigenvalues. This method treats the valence electrons as Slater orbitals and used parameters which are fitted empirically [1]. This new version of CNDO can be utilized on any element in the periodic table whose atomic number is less than or equal to 81. One fundamental difference between this method and the Pople method is the way it treats elements whose valence electrons are distributed over different subshells with different principal quantum numbers, which is illustrated by Figure 2-7. The molecule TO for example, where T is a transition element, would be treated as three atoms with T accounting for two of them at the same coordinate. If this treatment were carried over to the Lanthanides, where the valence electrons are dispersed over three subshells, we would have three atoms at the same coordinate (i.e.  $T_{(n-2)f}$ ,  $T_{(n-1)d}$ , and  $T_n$ ) [30]. Before the eigenvalues and eigenvectors of the various geometries of  $(MnO)_2$  could be determined, it was necessary to check the accuracy of the program by determining its ability to calculate dissociation energies of various diatomic molecules. The author

performed such calculations, which are listed in Tables 3-2 and 3-3. For those diatomic molecules which contain no transition elements, most of the calculated dissociation energies are in good agreement with experimental values, as seen in Table 3-2. When the dissociation energies of diatomics which contained either one or two transition elements are determined, there is very poor agreement between the calculated results and experimental values, as shown in Table 3-3. These results indicated that there is a problem in the way transition elements are treated. It was decided to modify those areas of the program which are a manifestation of treating the transition element as two atoms centered at one coordinate. One such area which needs to be modified is the computation of the atomic energies.

In M.O. theory the atomic energy is related to the dissociation energy by

$$E_{\text{dissoc}} \approx E_{\text{bond}} = E_{\text{tot}} - E_{\text{atomic}}. \quad (42)$$

Table 3-2  
Bond Energies and Lengths of Selected Diatomic Molecules.

| AB  | Bond Length<br>(Å) | Exp. <sup>a</sup> | Dissociation Energy<br>(eV) | Exp. <sup>a</sup> |
|-----|--------------------|-------------------|-----------------------------|-------------------|
| HF  | 1.00               | 0.92              | -6.01                       | -5.90             |
| LiH | 1.54               | 1.60              | -6.71                       | -2.50             |
| IH  | 1.63               | 1.61              | -4.47                       | -3.09             |
| CO  | 1.22               | 1.13              | -21.96                      | -11.09            |
| SnO | 2.25               | 1.84              | -1.46                       | -5.46             |

a) Ref [30]

Table 3-3  
Bond Energies and Lengths of Selected Diatomic Molecules which  
Contain one or more Transition Elements.

| AB              | Bond Length<br>(Å) | Exp.              | Dissociation Energy<br>(eV) | Exp. <sup>a</sup> |
|-----------------|--------------------|-------------------|-----------------------------|-------------------|
| Mn <sub>2</sub> | 2.8                | 3.4 <sup>b</sup>  | -286.18                     | -0.23             |
| FeO             | 1.58               | 1.57 <sup>a</sup> | -142.17                     | -4.20             |
| FeS             | 1.90               |                   | -149.5                      | -3.31             |
| MnBr            | 2.3                |                   | -108.                       | -3.22             |
| Fe <sub>2</sub> | 2.7                |                   | -179.24                     | -1.06             |

a) Ref. [31] b) Ref. [32]

Since the transition element is being treated as two atoms it is necessary to compute two atomic energies, as shown by

$$AE = s \cdot \text{ENEG}(s) + p \cdot \text{ENEG}(p) + (TE^2 \cdot \Gamma(I, I)/2) + d \cdot \text{ENEG}(d). \quad (43)$$

The ENEG terms are equal to the average of the ionization potential and the electron affinity of the respective subshell. TE is the total number of electrons and s, p, and d are the number of s, p, and d electrons respectively. The  $\Gamma(I, I)$  term is the monocenter coulomb repulsion for either the s or d subshell. The total atomic energy is then computed by adding the "atomic energy" of the s and d shells together. The program is modified to compute one atomic element per transition atom and this is done by determining the probability

of a valence electron being either an s (i.e. s/TE) or a d (i.e. d/TE). The equation utilized is

$$AE = s^*ENE(s) + p^*ENE(p) + ((s/TE)^2 * \Gamma(l,l)/2.) + ((d/TE)^2 * \Gamma(l,l)/2.) + d^*ENE(d). \quad (44)$$

The effect of this modification on the diatomic molecules containing transition elements is shown in Table 3-4. The reason that these diatomics are chosen to test the accuracy of the program is that they represent the two types of bonds that are encountered when the eigenvectors and eigenvalues of the (MnO)<sub>2</sub> cluster are being determined (i.e. the T-T and T-O types where T is a transition element).

Table 3-4  
Results of atomic energy modification to CNDO/2U on selected diatomics which contain one or more transition elements.

| AB              | Bond Length(A) | Dissociation Energy (eV) | Exp.(eV) |
|-----------------|----------------|--------------------------|----------|
| FeO             | 1.58           | 40.9                     | -4.20    |
| Mn <sub>2</sub> | 2.80           | 1.0                      | -0.23    |
| MnO             | 1.70           | 38.0                     | -3.70    |
| Fe <sub>2</sub> | 3.0            | -4.52                    | -1.06    |
| FeS             | 1.90           | 33.02                    | -3.31    |
| MnS             | 2.00           | 30.9                     | -2.85    |

For molecules representing the T-T bond, (i.e. Mn<sub>2</sub> and Fe<sub>2</sub>) there is good agreement between data and calculated results. For molecules

representing the T-O type bond however, there is poor agreement. This makes it necessary to modify the program so that it calculates a lower total energy for T-O and T-S bonds.

Another part of the algorithm which can be modified is that part which computes the coulomb repulsion matrix. This matrix is a set of values which represent the electrostatic repulsion between the charge clouds occupied by the electrons in the system. Equation (28) is the formula for the electrostatic repulsion between electrons (1) and (2) distributed over orbitals  $i,j,k$  and  $l$ . When the approximations of CNDO are applied to (28), equation (34) results. CNDO calculates the average electrostatic repulsion between any electron on atom A and any electron on atom B instead of the electrostatic repulsion between orbitals. Therefore, one matrix element is calculated per atom pair. For a T-O type molecule the following 3X3 coulomb matrix is formulated.

|    | O              | 4s              | 3d              |
|----|----------------|-----------------|-----------------|
| O  | $\Gamma_{OO}$  | $\Gamma_{O4s}$  | $\Gamma_{O3d}$  |
| 4s | $\Gamma_{O4s}$ | $\Gamma_{4s4s}$ | $\Gamma_{3d4s}$ |
| 3d | $\Gamma_{O3d}$ | $\Gamma_{4s3d}$ | $\Gamma_{3d3d}$ |

and for a T-T type atom the following 4X4 matrix is formulated.

|    | 4s              | 3d              | 4s              | 3d              |
|----|-----------------|-----------------|-----------------|-----------------|
| 4s | $\Gamma_{4s4s}$ | $\Gamma_{3d4s}$ | $\Gamma_{4s4s}$ | $\Gamma_{4s3d}$ |
| 3d | $\Gamma_{4s3d}$ | $\Gamma_{3d3d}$ | $\Gamma_{3d4s}$ | $\Gamma_{3d3d}$ |
| 4s | $\Gamma_{4s4s}$ | $\Gamma_{3d4s}$ | $\Gamma_{4s4s}$ | $\Gamma_{4s3d}$ |
| 3d | $\Gamma_{4s3d}$ | $\Gamma_{3d3d}$ | $\Gamma_{4s3d}$ | $\Gamma_{3d3d}$ |

The relationship between the electronic energy and the coulomb integral matrix elements are seen by the equations derived from CNDO approximations to SCF theory (i.e. equations 38 and 38a). The term  $(Z_B \Gamma_{AB} - V_{AB})$ , which represents the potential difference between the core ( the nucleus and non-valence electrons) and the valence electrons of atom B, is set to zero as a result of CNDO approximations. A valence electron on atom A experiences no potential difference between these components of atom B, thus the possibility of its penetration into B is eliminated. Such a penetration would lead to a net attraction yielding a lower bond and dissociation energy between A and B. To modify the program so that a greater net attraction between A and B is realized, the term-  $Q_B \Gamma_{AB}$  is modified. This term represents the effect of the potential due to the total charge on atom B [11]. If  $\Gamma_{AB}$  is increased, the potential due to atom B (i.e. Mn or Fe) will be more negative. This increase would have the same effect as increasing  $V_{AB}$  which would make the potential of the core of B greater than the valence electrons of B. This should then cause a greater net attraction between A and B to develop, which is what is desired. By looking at the first matrix, it can be seen that  $\Gamma_{AB}$  are represented by  $\Gamma_{O3d}$  and  $\Gamma_{O4s}$ , both of which are bicenter. The problem is to determine by how much these elements should be increased. Possibilities exist that the best results might be obtained by multiplying the  $\Gamma_{O4s}$  and  $\Gamma_{O3d}$  by the same or different amounts. By the process of trial and error it has been determined that if each  $\Gamma$  value is multiplied by 1.1, the best fit between dissociation energy, ionization potential and equilibrium bond distance results. After applying the above

corrections to the original program, the values shown in Table 3-5 result. Increasing the bicenter matrix elements of a T-O molecule should have the effect of increasing the electron population in the overlap between the oxygen and the d orbitals of the transition element. This is substantiated by looking at the population matrix, calculated from the equation

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{\mu i}^* c_{\nu i}, \quad (45)$$

where the c's are the coefficients of the atomic orbitals. This matrix does indeed show an increased electron population in the overlap between the oxygen and the d orbitals.

Table 3-5

Final values for the bond lengths, dissociation energies and ionization potentials of selected diatomics after the atomic energy and coulomb integral modifications were made to CNDO/2U.

| AB              | Bond Length (Å) | Exp.              | Ionization Potential (eV) | Exp.               | Dissociation Energy (eV) | Exp.  |
|-----------------|-----------------|-------------------|---------------------------|--------------------|--------------------------|-------|
| FeO             | 1.40            | 1.57 <sup>b</sup> | -11.69                    | -8.71 <sup>a</sup> | -6.77                    | -4.20 |
| FeS             | 1.90            |                   | -5.02                     |                    | -0.50                    | -3.70 |
| Mn <sub>2</sub> | 2.80            | 3.4 <sup>e</sup>  | -7.08                     | -6.9 <sup>c</sup>  | 1.00                     | -0.23 |
| MnO             | 1.45            | 1.77 <sup>b</sup> | -8.06                     |                    | -5.68                    | -3.70 |
| Fe <sub>2</sub> | 3.00            |                   | -16.09                    | -6.30 <sup>e</sup> | -4.52                    | -1.06 |
| MnS             | 1.80            |                   | -11.53                    |                    | -10.16                   | -2.85 |

a) Ref [33]   b) Ref [31]   c) Ref [34]   d) Ref [35]   e) Ref [32]

### Construction of VBDOS curves

After the modifications were made to the program it was then possible to begin the acquisition of the eigenvalues and eigenvectors of various geometries of the formula  $(\text{MnO})_2$ . In order for the eigenvalues and eigenvectors of a given geometry to qualify for comparison with XPS valence band spectra, it is necessary for that geometry to pass the self consistency test-i.e. two successive iterations of the total electronic energy must agree to within 0.01 eV. To pass this test it was necessary that the program calculated a total electronic energy that was within 0.01eV of the previous value. The determination of suitable geometries was like the coulomb matrix modification, a trial and error process, but after a long and arduous process, six suitable geometries were found, which are illustrated by Figure 3-2.

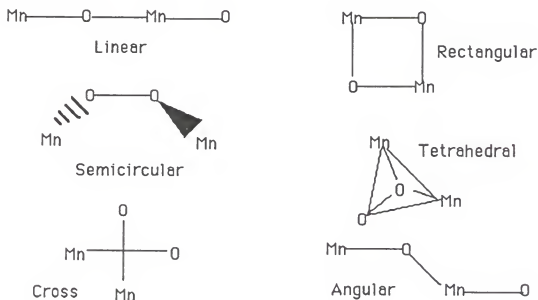


Figure 3-2. Suitable geometries for cluster  $(\text{MnO})_2$ .

After these geometries were determined, it was necessary to construct valence band density of states (VBDOS) curves from the eigenvalues and eigenvectors of each geometry. VBDOS curves are constructed by centering a Gaussian distribution function about each eigenvalue which has a FWHM of 0.85 eV (the natural line width for  $\text{AlK}\alpha$  radiation is this value) and then summing them over some specified energy range. The relative heights of the Gaussian distribution functions are determined by the following formula.

$$\text{Ht. of Gaussian} = \sum_j c_{ij}^2 \sigma_j \quad (46)$$

The  $c_{ij}$  's are the coefficients of the atomic orbitals and the  $\sigma_j$ 's are the Scofield cross sections [36]. A VBDOS curve has been constructed for each of the geometries shown in Figure 3-2. Figure 3-3 illustrates these VBDOS curves. Weighted distributions of these geometries can be used to construct composites. These simulate the effect of having active sites on the substrate surface which stabilize different geometrical configurations of the clusters. The weights simulate the relative fraction of each type of site on the surface. One such composite, which can be seen by Figure 3-4, shows a remarkable agreement with the lineshape obtained for very thick MnO supported on carbon foil. Although there is no evidence for 'geometry' selective active sites on the supports normally used for heterogeneous catalysts, there is also no evidence against such sites. Based on Figure 3-4, the variation in the molecular geometry for a given value of X does have an effect on the VBDOS. Valence band broadening is not only due to an increase in the number of atoms in a

cluster, but can also be due to the formation of a distribution of geometries of different stability on the surface. Thus a meaningful interpretation of the experimental VB DOS curves of supported metal oxide particles cannot be made without supplementary information on the particle size distribution.

Figure 3-3. Valence band density of states for self-consistent conformations of  $(\text{MnO})_2$ .

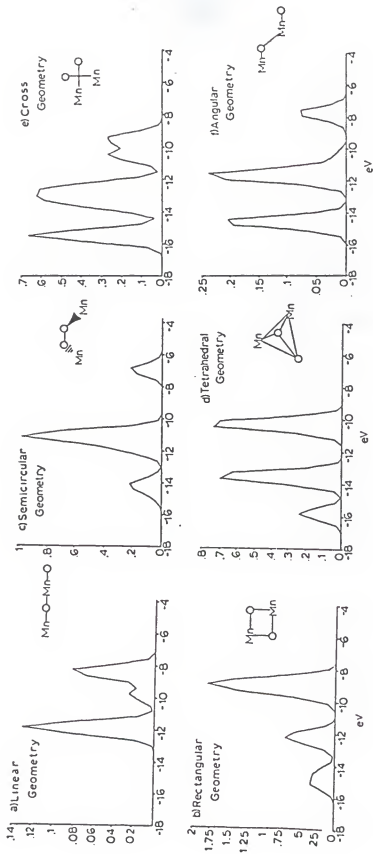
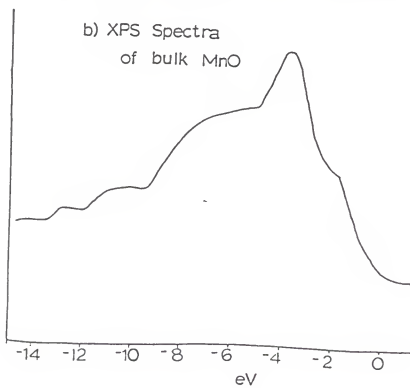
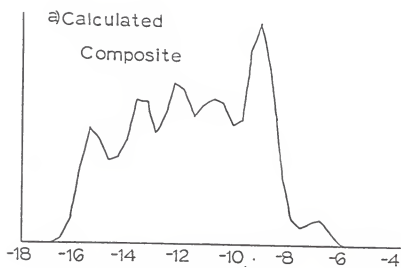


Figure 3-4. Valence band density of states of a calculated  $(\text{MnO})_2$  composite compared to spectrum of a continuous film of MnO.



## CHAPTER 4

### PHOTOEMISSION STUDIES OF VAPOR DEPOSITED AND SOLUTION DEPOSITED MANGANESE OXIDES AND SOLUTION DEPOSITED IRON OXIDES ON CARBON FOIL

#### Introduction

A large number of heterogeneous catalysts are composed of a material (e.g. a metal like Pt or Pd) which has been dispersed upon an inert support like silica, alumina, or carbon. These dispersed substances can be characterized by x-ray photoelectron spectroscopy. More specifically, XPS can be used to determine the relative concentrations of the various constituents and the relative particle size distributions of the supported material. The relative concentrations of the various constituents on a surface are determined by determining the relative peak areas of the constituents concerned. This then allows a value for the number atom ratio of one constituent atom to another to be computed. The effect of differences in the relative particle size distributions of the supported material can be qualitatively determined from shifts in binding energy within a given region. Such effects may be observed in both the core level regions and in the valence band regions. Valence band distribution narrowing is one of the most dramatic changes which can occur. Zhao and Young [28] prepared carbon surfaces containing submonolayers of MnO, as confirmed by

the relative concentrations of the constituents on the surface. Changes in the electronic structure which accompany reduction in the particle size distributions are determined for the highly dispersed MnO by comparing its valence band region with that of the bulk oxide. In that investigation, the oxide was prepared by vapor deposition. The number atom ratios calculated from XPS data indicated a low coverage (represented by  $\Phi$ ) for the dispersed oxide (the assumption is made that the lower the coverage value, the more highly dispersed is the oxide). It is also shown that it is possible to form a thick continuous film of the oxide on the carbon foil when a number atom ratio (i.e.  $N_{Mn}/(N_C+N_{Mn})$ ) of 1.0 is achieved at take off angles between 0 and 50 degrees. The effect of changes in the particle size distribution consisted of shifts in the position of the maximum of core, Auger and valence level spectra and a narrowing of the valence band level. This chapter will report results of similar experiments on other dispersed oxides of manganese and on dispersed ferric oxide. These characterizations are based on data acquired from samples prepared by vapor deposition and solution deposition. Because in solution deposition it might be possible for the oxide particles to diffuse in from the edge of the carbon foil, it is necessary to also perform quantitative analyses of samples which have had 0 edges, 1 edge and 2 edges directly exposed to the solution which is used in the solution deposition method in addition to the normal sample which has 4 edges directly exposed.

### Variable Angle XPS (VAXPS)

In the introduction of this chapter the term take off angle is mentioned. The take off angle is the angle between the electron analyzer and the sample, which is commonly denoted by the Greek letter  $\theta$ . The angle  $\theta$  is varied in almost any quantitative analysis undertaken, because its variation causes a variation in the effective mean electron escape depth, which is more commonly referred to as the probe depth. The mean electron escape depth is the average distance a photoelectron will travel before it undergoes an inelastic collision, a collision whereby it loses energy from the initial energy acquired from the photoemission process. Unfortunately inelastic collision is the fate that awaits most photoelectrons which are generated. This is what severely limits the depth that one can investigate in XPS.

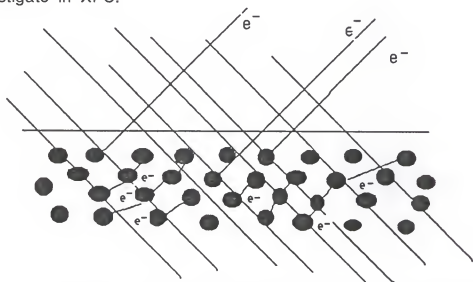


Figure 4-1. Schematic showing the attenuation of the incident x-ray radiation. The distance the photoelectron can travel before it suffers inelastic collision is quite short compared to the distance the x-ray can travel.

This is illustrated schematically in Figure 4-1. The distance the x-rays can travel into the solid is much greater than the photoelectrons can travel. The relationship between the mean and the effective mean electron escape depth is illustrated in Figure 4-2. Even though the mean electron escape depth is constant, the probe depth, or the effective mean electron escape depth becomes smaller as the take off angle becomes smaller until at a take off angle of 0 degrees, the photoelectrons generated are originating from the top monolayers of atoms only. Conversely at a take off angle of 90 degrees, the spectra that are obtained are the most "bulklike". The value of the effective mean electron escape depth depends upon the substance that is being analyzed. For metals this depth can be as small as 10 Angstroms. To change the take off angle in the KRATOS XSAM 800, one simply rotates the sample probe.

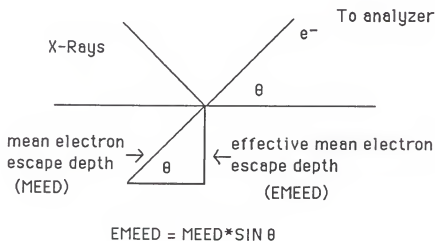


Figure 4-2. Diagram showing the relationship between the take off angle and the effective mean electron escape depth.

### Quantitative Analysis by XPS

XPS investigations often require that the relative concentrations of the various components of a surface be determined. If one averages over depth, then these relative concentrations can be expressed as number atom ratios (i.e.  $N_x/N_y$ ) which can be calculated from the following equation.

$$N_{x,i}/N_{y,j} = (I_{x,i}/I_{y,j}) (\sigma_{y,j}/\sigma_{x,i}) (\lambda_y(E_j)/\lambda_x(E_i)) (F(E_j,E_a)/F(E_i,E_a)) \cdot (T(E_j/E_a)/T(E_i,E_a)) \quad (47)$$

The  $I$ 's are the time normalized intensity ratios, the  $\sigma$ 's are the asymmetry corrected photoionization cross sections,  $E_i$  and  $E_j$  are the kinetic energies of photoelectrons  $i$  and  $j$  respectively and  $E_a$  is the analyzer pass energy. The subscripts  $x$  and  $y$  are the specific elements and subscripts  $i$  and  $j$  represent specific levels in  $x$  and  $y$  respectively [37].  $\lambda(E_i)$  is the inelastic mean escape depth,  $F(E_i,E_a)$  is the electron optical factor and  $T(E_i,E_a)$  is the analyzer transmission function. Fortunately experimentation has given results which allows equation 47 to be simplified. It has been shown that the product of the electron optical factor, the analyzer transmission function and the inelastic mean escape depth cancel each other [38]. The simplified form of equation 47 is

$$N_{x,i}/N_{y,i} = (I_{x,i}/I_{y,i}) (\sigma_{y,i}/\sigma_{x,i}) \quad (48)$$

If the elements  $x$  and  $y$  have not been recorded with identical window widths, then the window width must be incorporated into equation 48.

$$N_{x,i}/N_{y,i} = (I_{x,i}/I_{y,i}) (\sigma_{y,i}/\sigma_{x,i}) (W_x/W_y) \quad (49)$$

The number atom ratio evaluated at  $\theta=0$  degrees is an estimate of the coverage ( $\Phi$ ). The determination of the relative concentrations of the various constituents of a sample is made relatively simple with the DS800 software. After the spectra are acquired, the operator constructs the desired window that needs to be quantified and then simply types either "Q/A" or "Q/I" at the prompt, where "Q/A" means quantify area and "Q/I" means quantify intensity. To quantify area, "The peak area is calculated by summing the counts at all energies within the appropriate window, multiplying by the energy step between the channels and dividing by the total time spent acquiring each channel (i.e. the dwell time)" [39]. The quantification of peak intensity is determined by computing the difference between the most intense and the least intense channels within the spectral window, which is divided by the dwell time. The dwell time is another name for time normalization that was mentioned at the beginning of this section. Time normalization ensures that the quantities obtained are not affected by the operators choice of acquisition parameters. The atomic concentration % is then calculated from equation (50).

$$\left[ (x_i/q_i) / \sum (x_i/q_i) \right] \times 100. \quad (50)$$

The variable  $x_i$  is the ratio of the raw area/intensity of the  $i^{\text{th}}$  peak and  $q_i$  is the corresponding quantification factor (i.e. related to  $\sigma$  which was discussed earlier). The quantification factor or  $\sigma$  is a term which is a manifestation of how sensitive the instrument is to an electron in a particular orbital. The quantification factor is a function of the size of the atomic orbital.

Not only is the relative concentration of elemental constituents which comprise a surface desired, but also the relative concentrations of different chemical species which are contributing to a given spectral window (i.e.  $O_{1s}$ ,  $C_{1s}$ ). Analysis of a given photoelectron peak is achieved by peak fitting a number of different symmetrical line shape functions (either Gaussian or Lorentzian) to the peak. With the DS 800 software it is possible to express a distribution as a combination of a Gaussian and Lorentzian function. The distribution can be made to have as much as 50% Lorentzian character. To fit these distribution functions to a photoelectron peak, it is first necessary to construct a synthetic window (a different type of window than needed to determine the relative atomic concentrations). The synthetic window is first constructed by typing "syn" at the prompt. After the operator states the name of the window (i.e.  $C_{1s}$ ,  $O_{1s}$  etc.) the cursor appears and the window width is determined by pressing the space bar at the desired positions (in eV) at the beginning and the end of the window. After the window is formed a table appears which requires the operator to state what type(s) of function(s) are to be fit, (i.e. either Gaussian or Lorentzian or combinations thereof), the element IDs, the positions of maximum intensity of the component distributions and

the beginning and ending of a given distribution. Some degree of estimation and guesswork is required here and it takes practice for the operator to become proficient. In addition the operator can require the computer to fit a given distribution to within a given FWHM. After this is done, the interactive synthesis option is selected and the spectral window that the peak fit is being performed upon appears in the upper right portion of the display that appears. The background is subtracted out and the distributions that the operator selects appear under the photoelectron peak. The degree of fit is displayed, which at this point is usually very high. Next, the autofit command is utilized by typing "au" at the prompt. The computer fits the distributions selected to the peak, calculates the final fit value and displays it. The lower the value of the fit, the better it is. Figure 4-3 is an example of four distributions being fit to the  $O_{1s}$  region of four year old carbon foil, for which the  $O_{1s}$  contamination can not be completely eliminated.

### Preparation of Samples

As is mentioned in the introduction section of this chapter, vapor and solution deposition are utilized to prepare dispersed manganese oxides on carbon foil, while the ferric oxide samples are prepared by solution deposition only. To vapor deposit a manganese oxide onto carbon foil, it is first necessary to vaporize the manganese. Vaporization of the manganese is achieved by heating it resistively in a tungsten filament basket. The vapor produced is allowed to impinge upon a piece of carbon foil which is cut into a

Figure 4-3. Peak fit of the O1s photoelectron peak of carbon foil not subject to deposition by MnO<sub>2</sub> (clean carbon foil). The take off angle is 0 degrees.

#CLEAN CARBON FOIL. O1S REGION. THETA=0 DEGREES.

Run: 20CF05 Reg: 1  
Scan: 1 Chans: 157

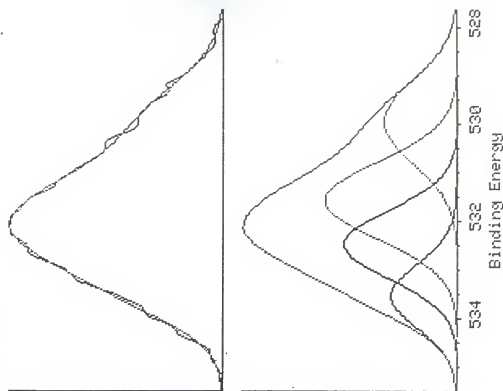
Start eV: 535.50  
End eV: 527.65

Fit: 1.7

100% Intensity: 579.  
100% Area: 39042.

Line Elmt. Energy Int. FWHM Area

|       |     |       |      |     |      |
|-------|-----|-------|------|-----|------|
| 1or10 | o1s | 533.5 | 31.0 | 1.6 | 15.2 |
| gauss | o1s | 532.5 | 52.9 | 1.6 | 27.5 |
| gauss | o1s | 531.6 | 61.6 | 1.9 | 35.9 |
| gauss | o1s | 530.0 | 34.3 | 2.0 | 21.5 |



rectangle with dimensions of approximately 1 cm X 1.2 cm. This is done in a sample analysis chamber of a Hewlett Packard X-ray photoelectron spectrometer at a base pressure of  $\sim 10^{-7}$  torr. Figure 4-4 illustrates that after the Mn is vaporized, it reacts with oxygen to form either the Mn(II) or Mn(III) oxide, depending upon the reaction conditions. These samples are outgassed by heating them to 235° C for 20 minutes before recording spectra. If there is any MnOOH on the surface, this procedure will convert it into  $\text{Mn}_2\text{O}_3$ . Dispersed manganese dioxide on carbon foil is prepared by solution deposition since it has been shown that  $\text{MnO}_2$  can be deposited by means of the  $\text{KMnO}_4$  decomposition [40]. Absence of  $\text{KMnO}_4$  itself is confirmed by the absence of K core level peaks in the survey scans. The reaction for this decomposition is given by equation (51), where the fate of the negative charge has not been established.

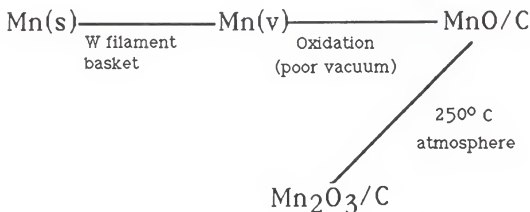
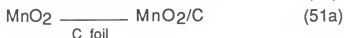


Figure 4-4. Schematic showing method of vapor deposition of manganese oxides on carbon foil.

Equation (51a) symbolizes deposition onto the carbon foil.



Solution deposition is accomplished by placing carbon foil rectangles into permanganate solution ( $\approx 3.3 \times 10^{-4} \text{ F}$ ) and allowing the dioxide to deposit. The samples are kept in solution for various lengths of times. Some were left in for 2 hours, some for 20 hours, and the remainder for 100 hours. To prepare the samples which contained either 0, 1, or 2 edges, a relatively large piece of carbon foil ( $\approx 5\text{cm} \times 5\text{cm}$ ) was placed in the permanganate solution for 100 hours. Figure 4-5 shows how the XPS samples with various edges exposed to the permanganate solution were selected after the 100 hours of deposition time. The rectangles were cut from the large rectangle with the use of a razor knife.

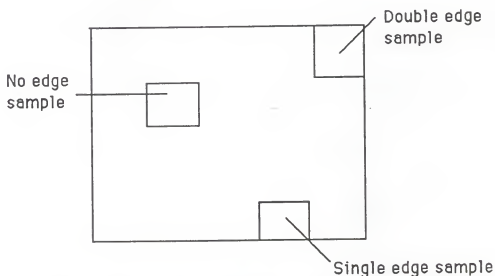


Figure 4-5. Diagram showing how samples containing the number of edges indicated were harvested after they were allowed to have  $\text{MnO}_2$  deposit on them for 100 hours.

Solution deposition of ferric oxide onto carbon foil necessitated the precipitation of the ferric ion out of solution before the carbon foil could be added. The precipitation was accomplished by adding a 1M

NaOH solution dropwise to a 0.1 N ferric nitrate solution. The NaOH was added until there was no further change in the appearance of the brown precipitate that was formed. The pH of the solution containing the precipitate at this point was 14. The carbon foil was then placed into the precipitate containing solution and the precipitate was allowed to deposit for either 18 or 100 hours. After the time allowed for the deposition to occur had expired the samples were washed alternately with de-ionized water and acetone. The samples resulting from manganese oxide deposition were also washed after deposition. The acetone facilitated the removal of any organics on the surface and aided in drying. Prior to letting either the Fe(III) or Mn(IV) oxide deposit onto the carbon foil, it is necessary to remove contaminant oxygen from the surface of the foil. According to the literature, this can be accomplished by heating the foil to 531° C in ultrapure nitrogen [41] or by heating it to 210°C in a vacuum [28]. Since the carbon foil is four years old, the oxygen peak could not completely be removed. Quantitative analysis of the above samples was performed after the acquisition of data by VAXPS. Regions in which data are acquired are the O<sub>1s</sub>, C<sub>1s</sub>, Mn<sub>2p</sub>, Fe<sub>2p</sub>, and the valence band (VB). It is also necessary to acquire data in the the regions just mentioned for the carbon foil not being subject to deposition of manganese dioxide. This allows the determination of the quantity of contaminant oxygen on the surface and comparison with carbon foil which has been subject to deposition. The valence band region is scanned from 15-0 eV.

## Results

After the carbon foil rectangles are placed in the permanganate solution for either 2, 20, or 100 hours, XPS data is acquired in the regions mentioned in the previous section. The  $O_{1s}$  region of the manganese free carbon foil is compared with the  $O_{1s}$  regions of the carbon foil samples which are subject to deposition to see if any deposition had occurred. Figure 4-3 shows a peak fit of the  $O_{1s}$  region of manganese free carbon foil acquired at a take off angle of 0 degrees. The manganese free carbon foil contains oxygens species in four different chemical environments. Several of the oxygen species have been identified in a paper written by Young [42]. The additional species are probably due to the fact that the carbon foil has aged. The carbon foil used by Young in the investigation to identify inherent surface oxygen species was new. The carbon foil used for the deposition of manganese dioxide is approximately 4 years old. Figure 4-6, which illustrates the  $Mn_{2p}$  peaks of a sample of carbon foil which has been allowed to soak in potassium permanganate solution 100 hours, confirms that manganese deposition has indeed occurred. Figure 4-7, which shows a peak fit for the  $O_{1s}$  region at a 0 degree take off angle for a sample prepared with 100 hours of deposition time, shows that there is an additional peak at 529.0 eV. This value compares very favorably with the literature value of 529.3 eV for the  $O_{1s}$  peak of bulk  $MnO_2$  [43]. The O/Mn ratio is 1.72, within experimental error of the expected ratio 2.0. Figure 4-8 illustrates a peak fit for the  $O_{1s}$  region of the same sample at a 85 degree take off angle. In this case, the O/Mn ratio is

Figure 4-6. Mn<sub>2p</sub> photoelectron peaks of a sample of carbon foil which was allowed to have MnO<sub>2</sub> deposit on it for 100 hours. These peaks were acquired at a take off angle of 35 degrees.

3rd CCF HEATED FOR 2 MO. 100HR MN02 DEP. THETA=35 DEGREES.  
Run: 3M1004 Reg: 4 (MN2P ) Scan: 1 Base: 16816 Max Cts/s: 421

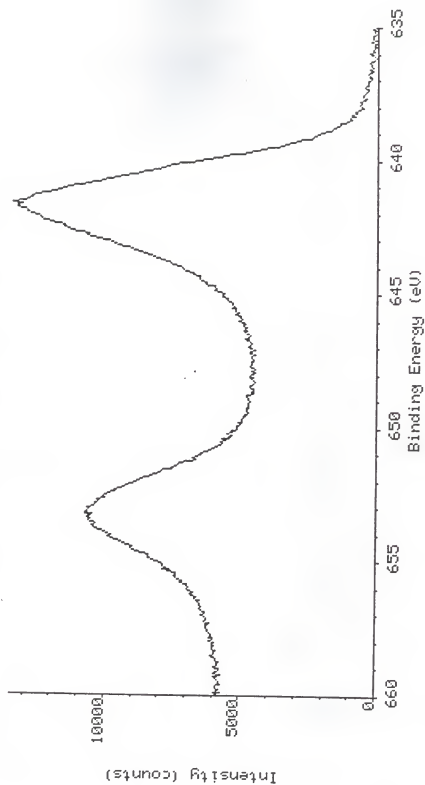


Figure 4-7. Peak fit of the  $O_{1s}$  photoelectron peak of a sample of carbon foil which was prepared by allowing  $MnO_2$  to deposit on it for 100 hours. The take off angle is 0 degrees.

4CLENN C FOIL WHERE NiO2 WAS DEPOSITED FOR 100HR. O1S REG. THETA=0 DEGREES.

Run: 3M1001 Reg: 2  
Scan: 1 Chans: 141

Start eV: 534.85  
End eV: 527.85

Fit: 2.4

100% Intensity: 576.  
100% Area 42867.

| Line      | Elmt. | Energy | Int. | FWHM | Area |
|-----------|-------|--------|------|------|------|
| gauss o1s |       | 533.0  | 49.5 | 1.7  | 23.9 |
| gauss o1s |       | 532.2  | 45.5 | 1.4  | 19.1 |
| gauss o1s |       | 531.4  | 54.7 | 1.5  | 22.6 |
| gauss o1s |       | 530.1  | 40.0 | 1.8  | 20.0 |
| gauss o1s |       | 529.0  | 44.9 | 1.3  | 15.8 |

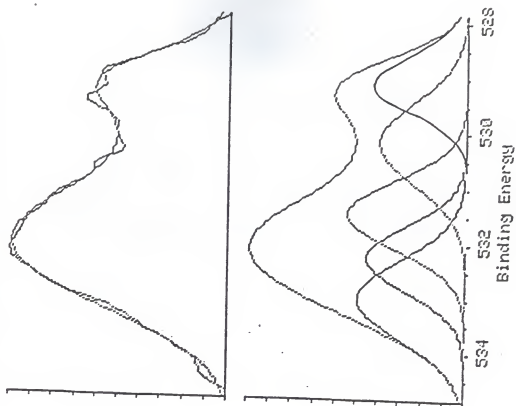


Figure 4-8. Peak fit of the O1s photoelectron peak for a sample of carbon foil which was prepared by allowing MnO<sub>2</sub> to deposit on it for 100 hours. The take off angle is 85 degrees.

\*CLEAN C FOIL WHERE NiO2 WAS DEPOSITED FOR 100HR. 01S REG. THETA=85 DEGREES.

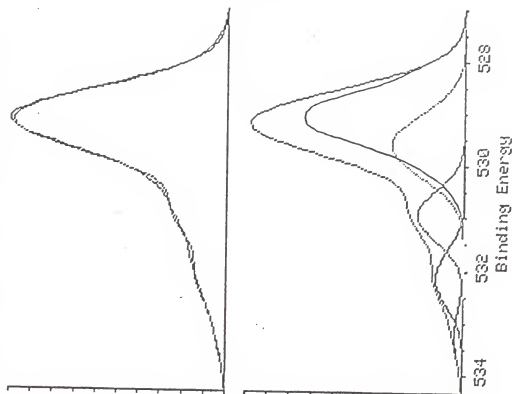
Run: 3M1006 Reg: 2  
Scan: 1 Chans: 148

Start eV: 534.35  
End eV: 527.00

Fit: 1.0

100% Intensity: 8632.  
100% Area: 360064.

| Line      | Elmt. | Energy | Int. | Fit/H Area |
|-----------|-------|--------|------|------------|
| Gauss 01s |       | 533.2  | 3.8  | 1.2        |
| Gauss 01s |       | 532.1  | 13.0 | 1.2        |
| Gauss 01s |       | 530.9  | 21.5 | 1.2        |
| Gauss 01s |       | 529.6  | 33.7 | 1.4        |
| Gauss 01s |       | 529.0  | 74.1 | 1.4        |



1.90. By comparison of the percent area values of the 529.0 eV distribution of Figures 4-7 and 4-8, it can be seen that deposited oxygen and therefore  $\text{MnO}_2$  is being incorporated into the layers of the carbon foil (i.e.  $\text{MnO}_2$  increases with increasing take off angle). This conclusion is substantiated by the number atom ratios  $N_{\text{Mn}}/N_{\text{C}}$  calculated at increasing values of the take off angle. As the angle is increased, the amount of Mn increased, as shown in Table 4-1. This is quite surprising since we expected to be able to form a continuous layer of the oxide at the surface like it was possible to do for vapor deposited  $\text{MnO}$  and  $\text{Mn}_2\text{O}_3$ . At  $\theta=0$  it is possible to form a continuous film of the vapor deposited manganese oxide [28], as shown in Table 4-2. It should be pointed out that the value of 1.00 is determined not by  $N_{\text{Mn}}/N_{\text{C}}$  but by  $N_{\text{Mn}}/(N_{\text{Mn}}+N_{\text{C}})$  in Table 4-2.

Table 4-1  
Values of  $N_{\text{Mn}}/N_{\text{C}}$  for solution deposited  $\text{MnO}_2$  on carbon foil.

| $\theta(\text{degrees.})$ | 2 hrs.           | 20 hrs.         | 100 hrs.        |
|---------------------------|------------------|-----------------|-----------------|
| 0                         | 0.055 ( $\Phi$ ) | 0.13 ( $\Phi$ ) | 0.073( $\Phi$ ) |
| 15                        | 0.13             | 0.20            |                 |
| 35                        |                  | 0.26            | 0.83            |
| 55                        | 0.046            | 0.22            | 1.24            |
| 85                        | 0.041            | 0.18            | 1.07            |

Table 4-2  
Coverage values for vapor deposited MnO and Mn<sub>2</sub>O<sub>3</sub>.

| OXIDE                          | $\Phi$                                 |
|--------------------------------|----------------------------------------|
| MnO                            | 0.18                                   |
| MnO                            | 1.00 (no discernible C <sub>1s</sub> ) |
| Mn <sub>2</sub> O <sub>3</sub> | 0.3                                    |
| Mn <sub>2</sub> O <sub>3</sub> | 0.65                                   |
| Mn <sub>2</sub> O <sub>3</sub> | 1.00 (no discernible C <sub>1s</sub> ) |

Solution deposition of ferric oxide on carbon foil gave similar quantitative results to that of the solution deposited manganese dioxide. Figure 4-9, which illustrates the Fe<sub>2p</sub> peaks of a carbon foil sample which was allowed to remain in the precipitated Fe solution (see preparation of samples section) for 100 hours, confirms that iron has indeed deposited onto the surface. In Figures 4-10 and 4-11, which are peaks fits of the O<sub>1s</sub> region of solution deposited ferric oxide on carbon foil at take off angles of 0 and 85 degrees respectively, a peak can be seen at 529.1 eV at 0 degrees and a peak at 529.2 eV at 85 degrees. This compares very favorably with a literature value of 529.3 eV for the O<sub>1s</sub> peak for the bulk Fe<sub>2</sub>O<sub>3</sub>. The O/Fe ratios for the sample analyzed at 0 and 85 degree take off angles are 1.8 and 1.6 respectively, within experimental error of the expected 1.5 for Fe<sub>2</sub>O<sub>3</sub>. There is incorporation of the oxygen from the iron oxide into the layers of the surface of the carbon, but the incorporation does not occur to the same extent as for MnO<sub>2</sub>. This conclusion is made from the 100% area values in Figures 4-10 and 4-11.

Figure 4-9. Fe2p photoelectron peaks of a sample of carbon foil which was allowed to have ferric oxide deposit on it for 100 hours.

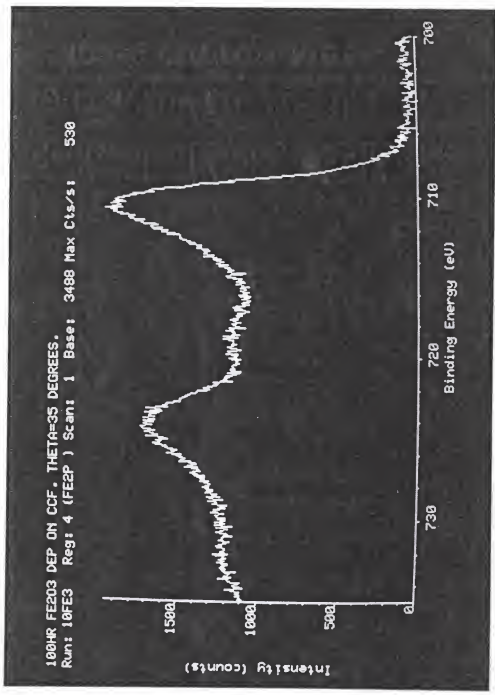


Figure 4-10. Peak fit of the O1s photoelectron peak for a sample of carbon foil which is prepared by allowing Fe<sub>2</sub>O<sub>3</sub> to deposit on it for 100 hours. The take off angle is 0 degrees.

Run: 10FE1 Reg: 3  
 Scan: 1 Chans: 153

Start eV: 534.60  
 End eV: 526.95

Fit: 1.6

100% Intensity: 3042.  
 100% Area: 196991.

| Line      | Elmt. | Energy | Int. | FWHM | Area |
|-----------|-------|--------|------|------|------|
| GAUSS 01S |       | 531.9  | 42.0 | 1.9  | 26.1 |
| GAUSS 01S |       | 530.7  | 47.0 | 1.6  | 24.7 |
| GAUSS 01S |       | 529.7  | 57.1 | 1.5  | 28.0 |
| GAUSS 01S |       | 529.1  | 41.2 | 1.5  | 20.2 |

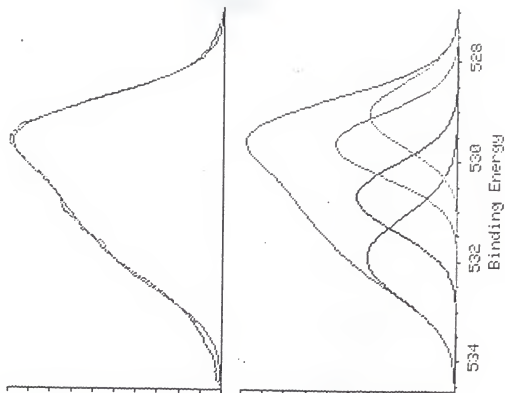


Figure 4-11. Peak fit of the O1s photoelectron peak for a sample of carbon foil which is prepared by allowing Fe<sub>2</sub>O<sub>3</sub> to deposit on it for 100 hours. The take off angle is 85 degrees.

#CCF WHERE FE2O3 WAS DEPOSITED FOR 100HR O1S REGION. THETA=55 DEGREES.

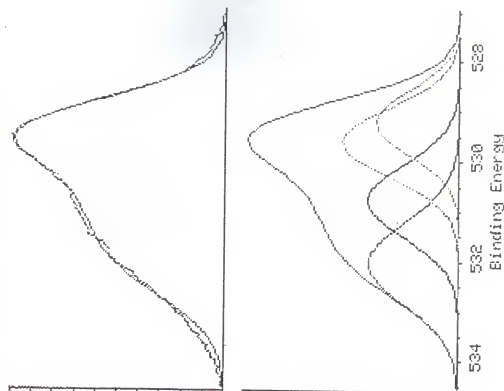
Run: 10FE2      Reg: 3  
Scan: 1      Chans: 153

Start eV: 534.60  
End eV: 526.95

Fit: 2.0

100% Intensity: 5536.  
100% Area: 354465.

| Line      | Elmt. | Energy | Int. | FNHM | Area |
|-----------|-------|--------|------|------|------|
| GAUSS 01S |       | 532.0  | 41.8 | 1.9  | 26.3 |
| GAUSS 01S |       | 530.8  | 42.4 | 1.7  | 23.9 |
| GAUSS 01S |       | 529.6  | 54.4 | 1.6  | 28.8 |
| GAUSS 01S |       | 529.2  | 38.7 | 1.5  | 19.3 |



At  $\theta=0$ , it is 196991 and at  $\theta=85$  it is 354465. If the second value for 100 % area is divided by the first a ratio of  $\approx 1.8$  is obtained. The same ratio for the  $\text{MnO}_2$  deposition yields a ratio  $\approx 8.4$ , an approximate 4 fold increase. The conclusion that ferric oxide is not being incorporated to as great a degree into the layers of the carbon foil as manganese dioxide can also be drawn from the area % of the 529 eV peak. At 85 degrees the 529 eV peak constitutes 52.9% of the area under the curve for the sample prepared by the solution deposition of  $\text{MnO}_2$  while it constitutes only 19.3% of the area under the curve for the sample prepared by the solution deposition of  $\text{Fe}_2\text{O}_3$ . The percentage of area contributed by the 529 eV peak is greater at  $\theta=0$  degrees than at 85 degrees for dispersed ferric oxide. This further substantiates the differences in the degree of incorporation between the two oxides. The number atom ratios also indicate that less of the oxide is being incorporated into the carbon foil. Table 4-3 gives the number atom ratios for the Fe and C atoms as resulting from solution deposition.

Table 4-3  
 $N_{\text{Fe}}/N_{\text{C}}$  values for samples prepared from the solution deposition of  $\text{Fe}_2\text{O}_3$  on carbon foil.

| take off angle | 18 hours | 100 hours |
|----------------|----------|-----------|
| 0              | 0.057    | 0.044     |
| 10             | 0.12     | 0.095     |
| 25             | 0.098    | 0.089     |
| 55             | 0.075    | 0.092     |
| 85             | 0.063    | 0.083     |

The photoemission results clearly show that there is a difference between the way that particles deposit from the vapor onto carbon foil and the way that particles deposit from solution onto carbon foil. The foil itself contains numerous gross defects, which are evident as microscopic tears from SEM photomicrographs. For a defect free foil, the surface monolayer would be expected to act as a barrier to deposition material, thus all particles would be confined to the top monolayer. It is obvious that particles can penetrate a defect-laden barrier. The extent of penetration might be expected to depend upon the particle deposition rate, the deposition time, and the defect density. Our results on vapor deposited manganese oxide particles show that the particles are confined mainly to the surface, and thus indicate that defect penetration is a minor process. This is expected because the particle dose (deposition rate multiplied by deposition time) is low and the defect density is small, as can be judged qualitatively from the fact that x-ray diffraction results show that the foil is semicrystalline. This means that it has more defects than a crystalline solid, and less defects than a polycrystalline solid. Thus, the probability that a particle deposits in a defect or that it deposits close enough to a defect to fall in from a random walk is expected to be small. Besides the possibility of a particle depositing through a defect in the surface, there is also the possibility that a particle can leave the surface of the carbon once it has been deposited. For the solution deposition of  $\text{MnO}_2$ , at least 4 scenarios can be envisaged, as follows:

- 1) Small particles of oxide produced by photodecomposition in the solution phase deposit on the surface and penetrate through defects.

- 2) Small particles of oxide produced by photoemission in the solution phase deposit on the surface and intercalate between layers of carbon by penetrating along exposed edges. They then can leave or "fall off" the carbon foil edges at a later time.
- 3) Permanganate anions intercalate the carbon foil and particles of  $\text{MnO}_2$  are produced by in-situ decomposition, while small particles produced by photodecomposition in solution phase deposit only on the surface.
- 4) Some combination of all three.

Photoemission results can be used to investigate these scenarios. Based on an earlier study of fresh carbon foil [42], the  $\text{O}_{1s}$  peaks at 532.1 eV and 533.2 eV may be associated with graphite oxide,  $\text{C}_x^+(\text{OH}^-)_y(\text{H}_2\text{O})_2$ , where the 532.1 eV peak is due to  $\text{OH}^-$  and the 533.2 eV peak is due to  $\text{H}_2\text{O}$ . For the four year old carbon foil, there is no significant difference between the ratios of the areas of  $\text{O}_{1s}$  peaks at 529.8 eV and 530.9 eV to the area of the  $\text{O}_{1s}$  peak at 532.1 eV for take off angles of 35 and 85 degrees, as shown in Figures 4-12 and 4-13. Thus, the subsurface has an almost homogeneous distribution of carbon oxidation species (the relative amount of the peak at 533.2 eV increases slightly with the take off angle) and segregating species in the depth explored. However after exposure of 4-year old carbon foil to dilute, neutral permanganate for 100 hours, the situation is that shown in Table 4-4. There are significant changes ( $> \pm 5\%$ ) in the peaks at 533.2 eV and 529.7 eV. Similar results are obtained in the case of the deposition of iron (III) as the hydrous oxide, which can be seen in Table 4-5. The drastic reduction in the

Figure 4-12. Peak fit of O1s photoelectron peak of carbon foil.  
The peak was acquired at a take off angle of 35 degrees.

#CLEAN CARBON FOIL. 01S REGION. THETA=35 DEGREES.

Run: 20CF06 Reg: 2  
Scan: 1 Chans: 160

Start eV: 535.55  
End eV: 527.60

Fit: 2.2

100% Intensity: 656.  
100% Area: 50640.

| Line  | Elmt. | Energy | Int. | FWHM | Area |
|-------|-------|--------|------|------|------|
| LOR10 | 01S   | 533.2  | 43.9 | 2.0  | 24.2 |
| GAUSS | 01S   | 532.1  | 64.4 | 1.7  | 30.1 |
| GAUSS | 01S   | 530.9  | 56.4 | 1.8  | 27.9 |
| GAUSS | 01S   | 529.5  | 33.8 | 2.0  | 18.0 |

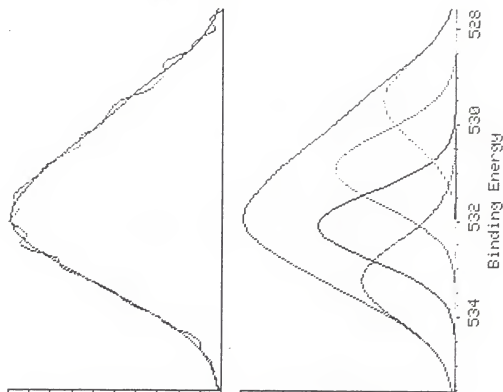


Figure 4-13. Peak fit of O1s photoelectron peak of carbon foil.  
The peak was acquired at a take off angle of 85 degrees.

\*CLEAN CARBON FOIL. O1S REGION. THETA=85 DEGREES.

Run: 20CF10 Reg: 2  
Scan: 1 Chans: 160

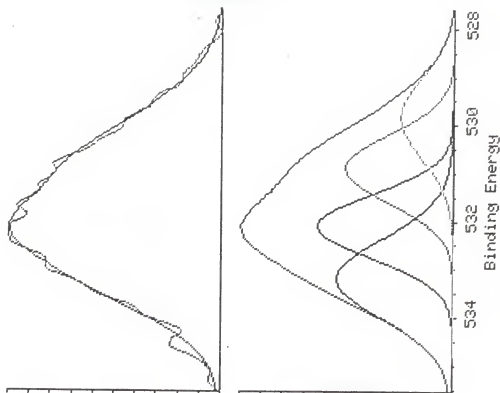
Start eV: 535.55  
End eV: 527.60

Fit: 2.8

100% Intensity: 588.  
100% Area: 42973.

Line Elmt. Energy Int. FWHM Area

|       |     |       |      |     |      |
|-------|-----|-------|------|-----|------|
| LOR10 | O1S | 533.2 | 54.6 | 2.0 | 31.8 |
| GAUSS | O1S | 532.1 | 63.6 | 1.6 | 28.6 |
| GAUSS | O1S | 530.9 | 51.0 | 1.7 | 24.4 |
| GAUSS | O1S | 529.8 | 24.9 | 2.0 | 14.3 |



533.2 eV peak is probably due to the dehydration of the surface caused by the evaporating acetone wash. The increase in the peak at 529.7 eV cannot be directly correlated to the amount of the deposit. There is a greater amount of deposited  $\text{MnO}_2$  than of deposited  $\text{Fe}_2\text{O}_3$  after 100 hours. The ratio of  $N_{\text{Mn}}/N_{\text{C}}$  to  $N_{\text{Fe}}/N_{\text{C}}$  is 12.9 at a take off angle of 85 degrees. The corresponding ratio of the change on  $\text{O}_{1s}$  at 529.7 eV, column 4- column 3, is 1.7. Thus, the increase in the species at 529.7 eV cannot be due to attack on carbon by  $\text{MnO}_4^-$  or  $\text{Fe}^{+3}$ , since it should be much larger in the case of  $\text{MnO}_4^-$  attack. If we regard each pair of planes of carbon as a "two wall cuvette", then they could entrain permanganate solution between them by capillary action provided the interplane separation is large enough. One would then expect to observe potassium peaks in the XPS spectra, but none are observed. It seems unlikely that  $\text{MnO}_4^-$  would be selectively drawn in, because of the charging problem. If the interplane separation is the same as that of the graphite, then both  $\text{K}^+$  and  $\text{MnO}_4^-$  are too large to be drawn in.

Table 4-4

$\text{O}_{1s}$  levels for carbon foil-- new [42], 4 year old (take off angle=85°) and after deposition of  $\text{MnO}_2$  for 100 hours on the latter ( take off angle=85°)

| Peak<br>BE (eV) | Relative % of Total Non Metal Oxygen |          |           | ASSIGNMENT     |
|-----------------|--------------------------------------|----------|-----------|----------------|
|                 | NEW                                  | 4-YR OLD | DEPOSITED |                |
| 529.7           |                                      | 14.3     | 51.3      | ?              |
| 530.9           |                                      | 24.4     | 26.9      | ?              |
| 532.1           | 60.0                                 | 28.6     | 16.9      | graphite oxide |
| 533.2           | 40.0                                 | 31.8     | 4.9       | bound water    |

Table 4-5

O<sub>1s</sub> levels for carbon foil-- new [42], 4 year old (take off angle=85°) and after deposition of Fe<sub>2</sub>O<sub>3</sub> for 100 hours on the latter (take off angle=85°)

| Peak<br>BE (eV) | Relative % of Total Non Metal Oxygen |          |           | ASSIGNMENT     |
|-----------------|--------------------------------------|----------|-----------|----------------|
|                 | NEW                                  | 4-YR OLD | DEPOSITED |                |
| 529.9           |                                      | 14.3     | 36.5      | ?              |
| 530.8           |                                      | 24.4     | 30.2      | ?              |
| 532.1           | 60.0                                 | 28.6     | 33.3      | graphite oxide |
| 533.2           | 40.0                                 | 31.8     | 0         | bound water    |

Thus scenario 3 is at best a minor process. Resolving the importance of this scenario would allow the catalysis results to be better addressed. Figure 4-5 illustrates how samples were prepared which have either 0, 1, or 2 edges exposed to the solution during the deposition process. It was stated that the samples were cut from the large rectangle of carbon foil with a razor knife. It is possible that the knife edge may have dislodged some of the manganese dioxide particles in the area of the cut. This is probably not a serious problem however since the x-ray beam is confined to the center of the carbon foil. The results of the "edge" experiment are shown in Table 4-6. The table indicates that an increase in the number of edges does not cause an increase in the amount of manganese oxide that is being incorporated in to the carbon foil. In fact, the opposite effect seems to be occurring. If scenario 1 is the major method for interlayer incorporation of MnO<sub>2</sub>, one would expect

the three samples to show the same distributions, because the defects are uniformly distributed. Thus, the results do not support the initial expectations for either scenario 1 or scenario 2. However reflection shows that these results could be obtained for either scenario 1 or scenario 2. Because the particles are more mobile at edges, in the 0 edge region, a particle must perform a sequence of directed "kicks" on a nearest neighbor in order to escape. However particles near an edge can easily fall off into the dilute colloid medium. If scenario 2 is occurring, then a decrease in the number of particles which have intercalated into the surface should be seen if the number of edges exposed to the permanganate solution is increased. Likewise, if particles are being uniformly incorporated into depths, they will be depleted more rapidly where 2 edges are available for escape and least rapidly where 0 edges are available for escape. Table 4-6 shows the largest number atom ratios for the 0 edge sample and the smallest number atoms ratios for the 2 edge sample. Thus, these results cannot distinguish between scenario 1 and scenario 2; many more experiments will be needed before the mechanism of particle incorporation can be established.

Besides being able to determine the relative concentrations of various constituents on a surface, XPS can also be used to study the electronic structure of particles on inert supports. The change in the electronic structure of these particles can be monitored by variations in the valence band density of states (VB DOS), which was discussed in the previous chapter. One of the variations which VB DOS undergoes when there is a change in the electronic structure

is a change in its width (FWHM). Changes in the FWHM can be attributed to three sources [27].

Table 4-6

$N_{Mn}/N_C$  values for solution deposited  $MnO_2$  on carbon foil with either 0,1, or 2 edges having been exposed to permanganate solution. (All samples were result of 100 hours of deposition time).

| $\theta$ | 0 edges | 1 edge | 2 edges |
|----------|---------|--------|---------|
| 0        | 0.15    | 0.079  | 0.12    |
| 35       | 0.32    | 0.17   | 0.18    |
| 55       | 0.33    | 0.18   |         |
| 85       | 0.29    | 0.21   | 0.13    |

1) An increase in the spin-orbit interactions from the renormalization of the d-electron wave functions in going from a free atom to a metal.

2) The splitting of atomic d levels by the crystal field into a doublet.

3) The mixing of the atomic levels throughout the Brillouin zone.

Items 2 and 3 are considered to be almost totally responsible for the increase of the FWHM with the increase in particle size. The two factors should also operate to increase the FWHM of nonmetals. Not only can changes in the electronic structure change the FWHM, but it can also change the value of the binding energy of the centroid region of the VBDOS ( $\epsilon_d$ ). This shift is brought about in metals by an increase in the d atomic orbital population when the supported atom undergoes transformation to the bulk material. For example, the

metals Pt and Pd have an electronic configuration of  $d^9s^1$  when they are supported by other atoms. However, the configuration changes to  $d^{9.6}s^{0.4}$  per atom for the bulk metal. The correlation between increased d electron population and the shift in the binding energy towards the Fermi level makes sense, since the electrons in the d atomic orbitals require less energy to undergo ionization. The reason for increased electron population in the d orbitals when an atom is part of the bulk material can be explained by renormalization of the Wigner-Seitz cell [27]. To achieve charge neutrality within this cell, the atomic wavefunction is truncated at the radius of the cell and the Wigner-Seitz sphere is renormalized. This renormalization places more charge outside the cell and thus causes more energy to be required to compress it. Since in transition metals ns orbitals are more diffuse than  $(n+1)d$  orbitals, most of the s electron population will reside outside the radius of the cell. When the atom undergoes the transition from atom to bulk, the compression of the atoms will require less energy if the electrons shift into the d atomic orbitals. This shifting lessens the amount of charge external to the Wigner-Seitz cell, thus making its compression easier. This shifting of electrons into the d atomic orbitals from the s atomic orbitals may be of importance in understanding catalytic reactions which show increased rates with decreasing coverage because it is believed that d electron vacancy is related to catalytic activity. Thus the dispersed material by the virtue of having less electrons in the d orbitals should have greater catalytic activity. An example is Ni deposition from solution. The

reaction proceeds spontaneously when small Pt clusters are used and then becomes completely quenched at higher Pt coverages [27].

Variation in the electronic structure of highly dispersed MnO on carbon foil can be seen when its VBDOS is compared to that of a thick continuous film of the oxide, which can be seen in Figure 3-1. The important thing to notice is that the VBDOS for the dispersed Mn(II) oxide is narrower and the binding energy of the centroid region has shifted away from the Fermi level. If indeed the theory discussed in the preceding paragraph is correct, then there is an increased s electron population in the Mn of the dispersed oxide particles as compared to the bulk oxide. The variation in the electronic structure of highly dispersed  $\text{Mn}_2\text{O}_3$  on carbon foil is similar to that of MnO when the VBDOS of the dispersed Mn(III) oxide is compared with its bulk oxide. This variation can be seen by looking at Figure 4-14. Note the spectra for two dispersed samples with coverages of 0.3 and 0.65. Since the VBDOS of the sample with a coverage of 0.3 is narrower than the VBDOS of the sample with a coverage of 0.65, there is apparently a difference in the electronic structure of these two samples also. Since the VBDOS is narrower for the samples with a coverage of 0.3, there is probably a larger s electron population in its Mn atoms, like in the highly dispersed MnO. For dispersed  $\text{MnO}_2$  on carbon foil, which unlike the previous oxides was prepared by solution deposition, dissimilar results were obtained. For dispersed  $\text{MnO}_2$ , there is not as great a shift in binding energy and not as great a change in the FWHM in its VBDOS relative to the bulk oxide VBDOS. These smaller changes can be seen in Table 4-7 and Figure 4-15. From these results, the particles are more

"bulklike" than the particles prepared by vapor deposition. This dissimilarity between particles prepared by solution deposition and vapor deposition is no doubt due to the vast difference between the two methods of deposition as opposed to the differences between the MnO, Mn<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub> oxides. In vapor deposition the Mn probably becomes highly dispersed when vaporized and impinges upon the foil in a highly dispersed fashion. In solution deposition, the MnO<sub>2</sub> may grow in solution before it becomes lodged to the carbon foil surface. It would be of interest to compare the catalytic activity of the dispersed oxide with its bulk counterpart to see if the presumed decreased d electron population found in Mn of the more dispersed oxides can affect the rate of a catalytic reaction. This is in fact the topic of the next chapter.

Table 4-7  
FWHM and binding energy values for dispersed and bulk Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>

| Oxide                                          | FWHM (eV)* | B.E.(eV)* |
|------------------------------------------------|------------|-----------|
| Mn <sub>2</sub> O <sub>3</sub> (coverage=0.3)  | 6.2        | 4.3       |
| Mn <sub>2</sub> O <sub>3</sub> (coverage=0.65) | 6.6        | 3.0       |
| Bulk Mn <sub>2</sub> O <sub>3</sub>            | 6.9        | 2.5       |
| MnO <sub>2</sub> (coverage=0.07)               | 6.3        | 4.5       |
| Bulk MnO <sub>2</sub>                          | 6.3        | 4.2       |

\* see Appendix

In conclusion, quantitative analysis of dispersed manganese oxides which were prepared by vapor deposition (i.e.  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}$ ) gave number atom ratios which indicated that the oxide particles stayed in the vicinity of the surface. This statement can be made because of the high coverage values at a take off angle of 0 degrees. Not only are the particles confined to the surface, but they are small enough to cause a change in the appearance in the valence band density of states and in addition shifts in binding energies of core level photoelectron peaks relative to the bulk oxide. Solution deposition gives completely different results. Number atom ratios show that the oxide particles diffuse into the layers of the carbon foil as time of deposition is increased. The particles which are solution deposited are larger than those which are vapor deposited. This may be due to the particle being able to grow in size in solution before it becomes lodged onto the surface of the carbon foil. This is especially true for solution deposited ferric oxide.

Figure 4-14. XPS spectra of dispersed and bulk  $\text{Mn}_2\text{O}_3$ .  
a) Highly dispersed oxide (coverage = 0.3);  
b) Less highly dispersed oxide (coverage = 0.65);  
c) Bulk  $\text{Mn}_2\text{O}_3$ .

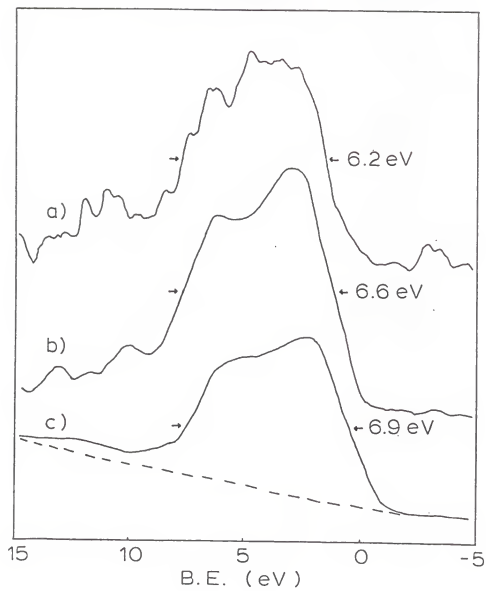
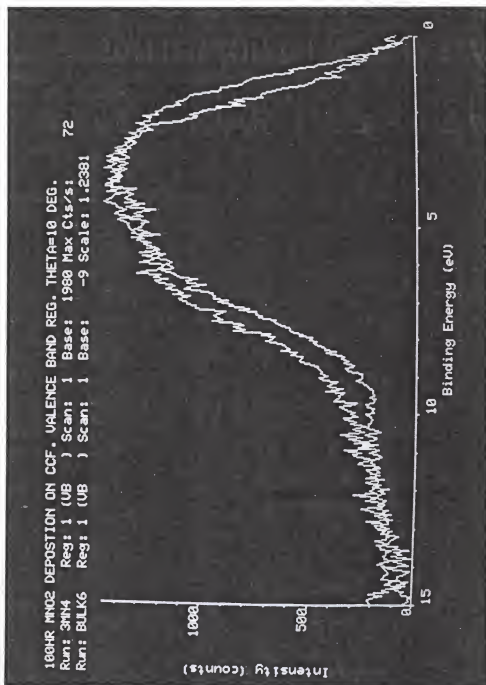


Figure 4-15. XPS spectra of valence band region of  $\text{MnO}_2$ . Spectrum with higher binding energy is that for dispersed  $\text{MnO}_2$  on carbon foil. The other spectrum is for bulk  $\text{MnO}_2$ .



## CHAPTER 5

### EFFECT OF DISPERSED MANGANESE OXIDES ON THE DECOMPOSITION OF PERMANGANATE SOLUTIONS

#### Introduction

Heterogeneous catalysts have been the subject of much research over the years. One of the largest users of this type of catalyst, the petroleum industry, is devoting considerable effort in order to improve catalyst performance and efficiency. At present the fabrication of heterogeneous catalysts is relatively imprecise, thus the field of heterogeneous catalysts has been referred to as a technologically advanced field without a sound scientific foundation [44]. A heterogeneous catalyst is one which is in a different phase than the reactants and products. The best example of such a catalyst is that of a catalytic converter in an automobile. In this case, substances in the gaseous phase (i.e. CO and unburned hydrocarbons) react with a catalyst in the solid phase. As a result of research conducted to improve performance, the catalytic substance is frequently dispersed on an inert support, in the form of clusters. The data acquired by XPS can be used to characterize clusters of deposited materials on inert supports. The data can be interpreted to obtain the number atom ratios of the catalytic substance to the

supporting substance (i.e.  $\text{NMn/NC}$  discussed in the previous chapter) at the surface by the acquisition of data at a take off angle of  $\theta=0$  and at various depths below the surface ( $\theta>0$ ). XPS can also be used to determine the particle size distribution. These two pieces of information can be correlated with the rate of the reaction the catalyst is enhancing. It is possible then to determine if the rate of the catalytic reaction is being affected due to the catalyst dispersion. In this chapter the results obtained when the decomposition of permanganate is carried out in the presence of dispersed  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  on carbon foil is discussed. It is necessary that the reaction be carried out in neutral solution because strongly alkaline or acidic solutions affect the rate of decomposition [45-46]. Light also affects the rate of decomposition of permanganate [47]. While  $\text{MnO}_2$  has been shown to catalyze the decomposition of permanganate [46], neither  $\text{Mn}_2\text{O}_3$  or  $\text{MnO}$  have been shown to catalyze its decomposition. However,  $\text{Mn(III)}$  in the solid is proposed as an intermediate in the propagation steps for the decomposition of manganate [48] and  $\text{Mn}^{+2}$  has been shown to react with permanganate in 3M  $\text{HClO}_4$  solution [49]. It seems reasonable that both  $\text{MnO}$  and  $\text{Mn}_2\text{O}_3$  can affect the decomposition of  $\text{MnO}_4^-$  even though they cannot be regarded as true catalysts. Fortunately, the kinetics of this decomposition are slow enough so as to allow spectrophotometric monitoring [47,50]. The electronic structure data reported in the last chapter will then be correlated with the catalytic activity (i.e. the rate of decomposition of permanganate solution) to determine the effect of dispersion on the rate of the decomposition reaction.

### Kinetics of Reactions

In this research project the relative amounts of catalytic reactivity for various samples of dispersed manganese oxides on carbon foil are reported. Catalytic activity affects the rate of reaction, which is defined as the "rate of change of concentration of a substance involved in the reaction with a minus or plus sign attached, depending on whether the substance is a reactant or a product" [51]. If we examine the equation given by



the rate of reaction can be defined by any of the following

$$-d[A]/dt, -d[B]/dt, +d[G]/dt, \text{ or } +d[H]/dt.$$

From the above relationships it can be seen that the rate of reaction is affected by the concentration of the components of the reaction. Usually, it is affected only by the concentration of the reactants. If the concentration of the products does affect the reaction rate, then the reaction is referred to as autocatalytic. If an equation is formed which shows the relationship between the rate of reaction and the concentration of a component, then that equation is a rate expression. The reaction of hydrogen and iodine to produce hydrogen iodine is given by



The rate expression for equation (53) is

$$d[\text{HI}]/dt = k[\text{H}_2][\text{I}_2], \quad (54)$$

where  $k$  is the reaction constant. It is not possible to derive the rate expression from the stoichiometric equation and therefore it must be determined as the result of experimentation. The order of a reaction is determined by summing the values of the exponents of the concentrations of the rate expression. The rate expression for the formation of HI is given by

$$d[\text{HI}]/dt = k[\text{H}_2]^1[\text{I}_2]^1.$$

The order of the reaction overall is simply the sum of all exponents of the concentrations. Each individual exponent is called the order with respect to that component. The above reaction is then first order with respect to hydrogen and first order with respect to iodine and second order overall. The rate constant  $k$  has dimensions of

$$[\text{conc.}]^{1-n} [\text{time}]^{-1}.$$

Commonly used units for the rate constant are moles/liter, moles/cc, molecules/cc, or pressure in mm Hg or in atmospheres. The preferred unit for time is seconds.

Since it is not possible to determine the rate expression from the stoichiometric equation, it is necessary to fit experimental data to a rate equation. The data is acquired by recording the decrease in concentration of a reactant over time. From the data, a curve is plotted of concentration vs. time. The rate of the reaction at any

particular time would be the negative of the slope of the curve. For the  $n$ th order reaction of a single component we have the following

$$-dc/dt = kc^n \quad (55)$$

after integration for  $n=1$

$$\ln(c_0/c) = kt \quad (56)$$

$$\text{or} \quad c = c_0 e^{-kt} \quad (57)$$

The data should then fit a plot of  $\log c$  vs.  $t$  in order for it to be a reaction which is first order overall.

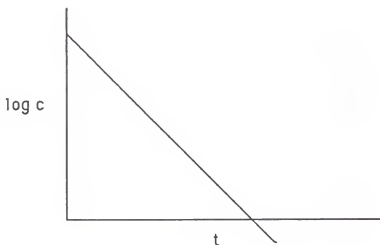


Figure 5-1. Linear plot for a first-order reaction.

For a second order reaction,  $n=2$  and the integrated form of the rate equation is

$$1/c - 1/c_0 = kt. \quad (58)$$

From the above equation, a plot of  $1/c$  vs.  $t$  should be linear, with a positive slope.

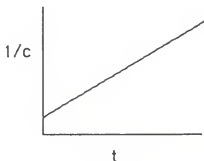


Figure 5-2. Linear plot for a second order reaction.

Data for a second order reaction should fit a plot as seen in Figure 5-2. The decomposition of permanganate solutions, which is the focus of this chapter, is an example of an autocatalytic reaction, where the rate of the reaction is affected by the amount of the manganese dioxide that is being produced. The decomposition of permanganate is represented by the following equation



It is not known where the electron is resident in equation (59) however [45]. Generically, an autodecomposition reaction can be represented by the equation



where A is the reactant and B is a product which catalyzes the reaction. The rate expression for such a reaction is given by

$$-dA/dt=k[A][B]. \quad (60)$$

If  $A_0$  and  $B_0$  equal the initial concentrations of A and B, then  $A_0 - A = B - B_0$  or  $B = A_0 + B_0 - A$ . If equation (60) is integrated the following rate expression results.

$$1/(A_0 + B_0) \ln (A_0 B / B_0 A) = kt \quad (61)$$

### Experimental

As was mentioned in the previous chapter, vapor deposition was used to prepare dispersed  $MnO$  and  $Mn_2O_3$  on carbon foil and solution deposition was used to prepare dispersed  $MnO_2$  on carbon foil. The carbon foil which was used as a support of these oxides was from Goodfellow metals and is assayed at 99.8% C. The foil is cut into rectangles with dimensions of 1 cm X 1.2 cm. There is oxygen contamination on the surface of this foil, which can be almost completely removed by heating to 2100°C in vacuum [28]. Some of the carbon foil that was used was four years old; not as much of its oxygen could be removed by heating. The method of vapor and solution deposition was discussed in the previous chapter and will not be repeated here. The coverages ( $\Phi$ ) (i.e.  $N_{Mn}/N_C$  at  $\theta=0^\circ$ ) of the oxides were determined by variable angle XPS. The names of the oxides and their coverages for the samples used in this investigation are listed in Table 5-1. A value of  $\Phi = 1$  means a continuous film of the oxide is present. This value is obtained only when no discernible  $C_{1s}$  peak is present for  $\theta \gg 0^\circ$ . No discernible  $C_{1s}$  peak was observed for a take off angle of 50 degrees. The composition of

these deposits are unchanged even after four months in a drybox filled with ultrapure nitrogen. It has been shown that MnO is quite stable to air exposure at room temperature for short periods of time [45,50,52].

Table 5-1  
Coverage ( $\Phi$ ) values for vapor deposited MnO and Mn<sub>2</sub>O<sub>3</sub> and solution deposited MnO<sub>2</sub> on carbon foil.

| Oxide                          | $\Phi$                                     | length of time for solution deposition |
|--------------------------------|--------------------------------------------|----------------------------------------|
| MnO                            | 0.18                                       |                                        |
| MnO                            | 1.00 (no discernible C <sub>1s</sub> peak) |                                        |
| Mn <sub>2</sub> O <sub>3</sub> | 0.23                                       |                                        |
| Mn <sub>2</sub> O <sub>3</sub> | 1.00 (no discernible C <sub>1s</sub> peak) |                                        |
| MnO <sub>2</sub>               | 0.055                                      | 2 hours                                |
| MnO <sub>2</sub>               | 0.133                                      | 20 hours                               |
| MnO <sub>2</sub>               | 0.073                                      | 100 hours                              |

In addition there are results for samples of dispersed MnO<sub>2</sub> on carbon foil which were prepared and studied four years ago, but for which the coverages were not determined. The effects of all of the samples listed in Table 5-1 upon the decomposition of permanganate solution are determined by placing them into a permanganate solution and measuring the absorbance of permanganate at 525 nm at 12 hour intervals for a total time of 48 hours. From this data plots

Figure 5-3. Absorbance versus time data for MnO and Mn<sub>2</sub>O<sub>3</sub> samples.

(o) permanganate solution; (●) permanganate solution + carbon foil; (+) permanganate + dispersed MnO on carbon foil; (X) permanganate solution + dispersed Mn<sub>2</sub>O<sub>3</sub> on carbon foil; (Δ) permanganate solution + thick Mn<sub>2</sub>O<sub>3</sub> on carbon foil.

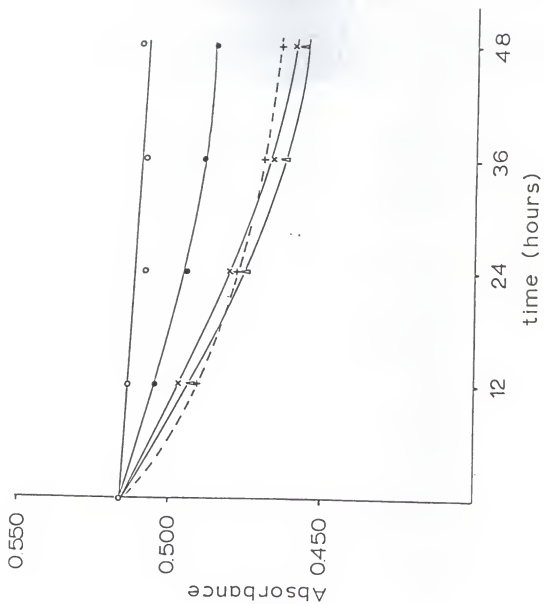


Figure 5-4. Absorbance versus time data for colloidal  $\text{MnO}_2$  deposited from a  $2.0 \times 10^{-4}$  F potassium permanganate solution.

(o) permanganate solution; (●) permanganate solution + 100 hour deposit; (+) permanganate solution + 20 hour deposit; ( $\Delta$ ) permanganate + carbon foil; (X) permanganate + 4 hour deposit; ( $\blacktriangle$ ) permanganate + 2 hour deposit.

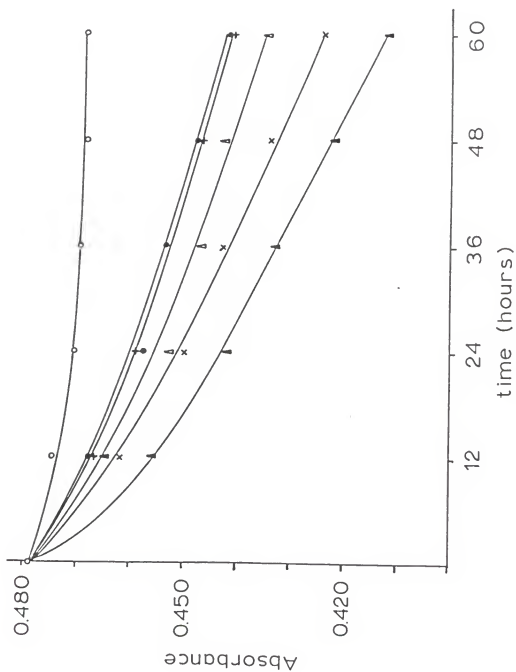
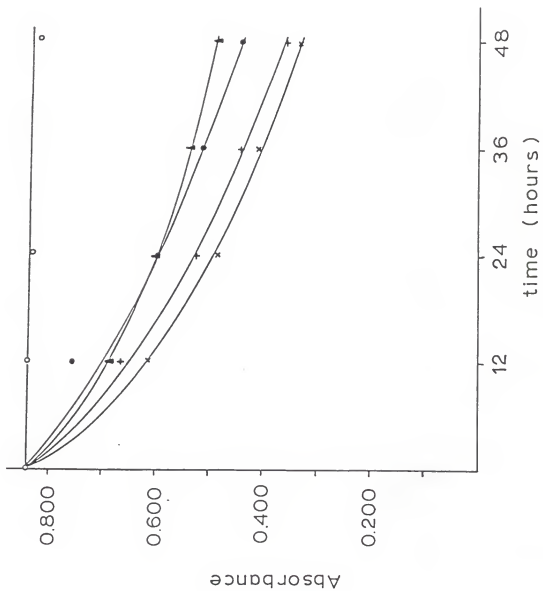


Figure 5-5. Absorbance versus time data for colloidal  $\text{MnO}_2$  deposited from a  $3.3 \times 10^{-4}$  F potassium permanganate solution.

(o) permanganate solution; ( $\blacktriangle$ ) permanganate + carbon foil; ( $\bullet$ ) permanganate + 20 hour deposit; (+) permanganate + 2 hour deposit; (X) permanganate + 100 hour deposit.



of absorbance versus time are constructed, which can be seen in Figures 5-3 to 5-5.

### Results

Before the raw data in Figures 5-3 to 5-5 can be interpreted, it needs to be normalized so the increase in the rate of decomposition due to the oxide alone can be realized. Two factors for normalization must be considered. The first factor is the differing concentrations of the permanganate solutions. The vapor deposited samples and the solution deposited  $\text{MnO}_2$  samples which were prepared four years ago were allowed to decompose a  $2.0 \times 10^{-4} \text{ F}$  permanganate solution while the freshly prepared  $\text{MnO}_2$  samples are allowed to decompose a  $3.3 \times 10^{-4} \text{ F}$  solution. The second factor which is factored into the normalized equation is the differing areas of coverage of the carbon foil with the oxide particles due to the differences in vapor and solution deposition. With solution deposition the oxide particles are covered on both sides while for vapor deposition, only a circular area of one side is covered. This can be seen by Figure 5-6. Because of this difference, the effective coverage is determined. Since in solution deposition both sides are being covered, the effective coverage is equal to the measured coverage. But for samples prepared by vapor deposition, the measured coverage must be multiplied by the area of the circle and divided by two times the area of one side of the carbon rectangle.

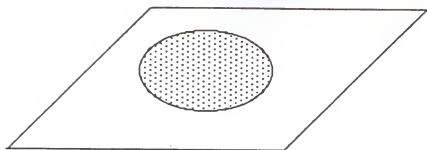


Figure 5-6. Illustration of vapor deposited oxide particles on one side of carbon foil.

Thus, the effective coverage is less than the measured coverage (i.e.  $\Phi_{\text{eff}} < \Phi$ ). By taking these two factors into account, it is possible to formulate an equation which is normalized for the catalytic effect due to the oxide alone. The normalized equation is given by

$$Y = |\Delta \text{abs}| / (\Phi_{\text{eff}} \cdot C_0). \quad (62)$$

$|\Delta \text{abs}|$  is the magnitude of the absorbance change due to the oxide alone,  $C_0$  is the initial concentration of the permanganate solution, and  $\Phi_{\text{eff}}$  has been defined above. Plots of  $Y$  vs.  $t$  (time) are shown in Figures 5-7 and 5-8. It has been determined that the data for  $\text{MnO}$  on carbon foil and  $\text{MnO}_2$  on carbon foil with a coverage of 0.073 can be fit with a high correlation to an equation of the form

$$Y = a \ln(t+1) + b \quad (63)$$

and the data for  $\text{Mn}_2\text{O}_3$  on carbon foil, bulk  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$  with coverages of 0.055 and 0.133 on carbon foil can be fit with high correlation to a linear equation of the form

$$Y=at+b. \quad (64)$$

Table 5-2 shows the values for a,b, and the degree of correlation when equations 63 and 64 are fitted to experimental data. The solid lines in Figures 5-7 and 5-8 correspond to the best fits.

Table 5-2  
Fit Parameters for Experimental Data.

| Sample                            | Equation 63 |       |       | Equations 64 |       |       |
|-----------------------------------|-------------|-------|-------|--------------|-------|-------|
|                                   | a           | b     | CORR  | a            | b     | CORR  |
| Dispersed MnO                     | 33.2        | -1.65 | 0.992 |              |       |       |
| Dispersed $\text{Mn}_2\text{O}_3$ | 43.4        | -16.6 | 0.913 | 3.89         | 5.32  | 0.991 |
| Thick $\text{Mn}_2\text{O}_3$     | 11.2        | -2.63 | 0.965 | 0.94         | 4.68  | 0.976 |
| Bulk $\text{Mn}_2\text{O}_3$      | 11.4        | -3.32 | 0.947 | 0.98         | 3.44  | 0.987 |
| $\text{MnO}_2$ ( $\Phi=0.055$ )   | 114         | -49.5 | 0.878 | 10.5         | 2.20  | 0.977 |
| $\text{MnO}_2$ ( $\Phi=0.073$ )   | 117         | -19.1 | 0.981 | 9.33         | 66.8  | 0.951 |
| $\text{MnO}_2$ ( $\Phi=0.133$ )   |             |       |       | 3.70         | -42.0 | 0.998 |

Figure 5-7. Normalized change in absorbance magnitude (see text) versus time for MnO and Mn<sub>2</sub>O<sub>3</sub> samples. The original is a point for each.

(o) dispersed Mn<sub>2</sub>O<sub>3</sub> on carbon foil; (●) dispersed MnO on carbon foil; (Δ) thick Mn<sub>2</sub>O<sub>3</sub> on carbon foil; (+) bulk Mn<sub>2</sub>O<sub>3</sub>.

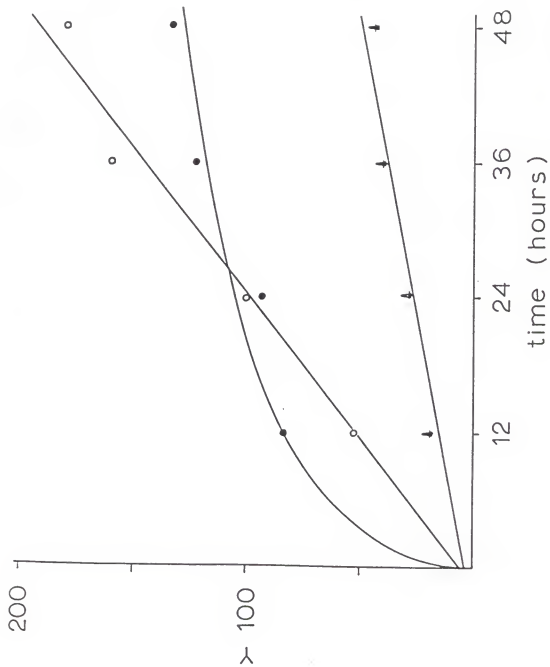
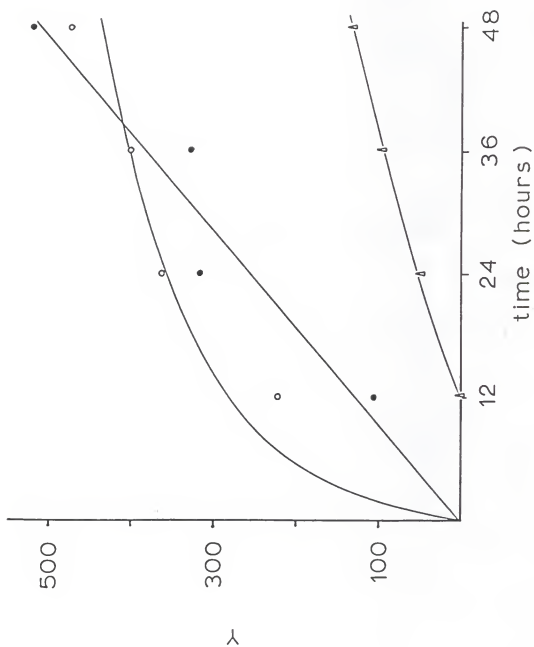


Figure 5-8. Normalized change in absorbance magnitude (see text) versus time for colloidal deposited  $\text{MnO}_2$ . The origin is a point for each.  
(o) 100 hour deposit; (●) 2 hour deposit; ( $\Delta$ ) 20 hour deposit.



### Correlation of Rate Law Expressions with Experimental Data

One can investigate the fit of various rate law expressions to the experimental data. Since the decomposition of neutral permanganate in the absence of carbon supported manganese oxide particles is autocatalytic with colloiddally dispersed  $\text{MnO}_2$  particles catalyzing the reaction, it is reasonable to assume that the decomposition remains autocatalytic in the presence of carbon supported manganese oxide particles. Unfortunately, such a fit cannot be made directly, because the activity of permanganate is not known. Nevertheless it is possible to simulate data from a second order autocatalytic reaction and to explore the limiting behavior of such a reaction. Equation (61) requires initial values for the concentrations of  $A_0$  and  $B_0$ . Arbitrary values of 1.00 M are chosen for  $A_0$  and 0.20 M is chosen for B. Recalling that  $A_0 - A = B - B_0$  and by the substitution of the values chosen for  $A_0$  and  $B_0$  into equation 61, we have the following the equation given by

$$(1/1.2)\ln(5B/A)=kt.$$

By knowing  $t$  and  $k$ , one can solve for  $5B/A$ , which represents one equation with two unknowns. If  $A_0 - A = B - B_0$ , then  $1.00 - A = B - 0.20$ . There are now two equations with two unknowns, and  $A$  and  $B$  can be uniquely determined. Knowing  $A$  and  $A_0$  for each value of time  $t$ , the quantity  $|A - A_0|/A_0$  can be determined for each value of  $t$ . The relationship between  $t$  and  $|A - A_0|/A_0$  can be fit with high correlation to the following linear functions

$$|A-A_0|/A_0 = a \ln (t+1) + b \quad (65)$$

when  $k$  is large and

$$|A-A_0|/A_0 = at + b \quad (66)$$

when  $k$  is small.

The values for  $a$ ,  $b$ , and the degree of correlation for a given rate constant  $k$  are shown in Table 5-3. Thus in fact, the empirical fits to the experimental data can be regarded as limiting forms of a 2<sup>nd</sup> order autocatalytic reaction.

Table 5-3

Example of 2<sup>nd</sup> order Autocatalytic Simulation for various Rate Constants on Time Intervals Corresponding to Those Used Experimentally.

$$A_0 = 1.00 \text{ M}; B_0 = 0.20 \text{ M}$$

| Rate Constant(hr <sup>-1</sup> ) | Equation 65* |        |       | Equation 66* |        |       |
|----------------------------------|--------------|--------|-------|--------------|--------|-------|
|                                  | a            | b      | CORR  | a            | b      | CORR  |
| 1/6                              | 0.271        | -0.005 | 0.990 | 0.020        | 0.241  | 0.874 |
| 1/12                             | 0.236        | -0.085 | 0.927 | 0.021        | 0.046  | 0.983 |
| 1/24                             | 0.138        | -0.070 | 0.858 | 0.013        | -0.021 | 0.998 |

\*Y=|A-A<sub>0</sub>|/A<sub>0</sub>

On the basis of the simulation results, the conclusion is made that the rate of reaction is greater in the presence of dispersed MnO particles than dispersed  $\text{Mn}_2\text{O}_3$  particles. Also the rate of reaction for carbon supported dispersed  $\text{Mn}_2\text{O}_3$  particles is greater than for thick continuous films of  $\text{Mn}_2\text{O}_3$  on carbon and for bulk  $\text{Mn}_2\text{O}_3$ . It is interesting that the curves for continuous film and bulk  $\text{Mn}_2\text{O}_3$  are coincident. This should be the case since thick film is expected to exhibit bulk behavior based on its electronic structure. The rates of reaction for  $\text{MnO}_2$  are probably too high. This may be due to the intercalated particles contributing to the catalytic activity, which are not accounted for in  $\Phi_{\text{eff}}$ . Presently experiments are being performed on other layered and unlayered solid supports to help clarify this situation. Figure 5-9 shows a proposed mechanism for the autodecomposition of neutral permanganate [48]. The role of the dispersed  $\text{Mn}_2\text{O}_3$  can be seen in steps 4 & 5. The  $\text{Mn(III)}$  allows the cycle to go from step 2 to 5 without having to go through step 4. As a result of this,  $\text{MnO}_2$  can build up faster. Since the concentration of  $\text{H}^+$  is low in neutral solution, it is advantageous that step 4 be avoided.

1.  $\text{MnO}_4^- \xrightarrow{h\nu} \text{MnO}_4^{*-} \xrightarrow{\text{radiationless relaxation}} \text{MnO}_4^{\neq-}$
2.  $\text{MnO}_4^{\neq-} + \text{MnO}_4^- \longrightarrow \text{MnO}_4^{-2} + \text{MnO}_2 + \text{O}_2(\text{g})$
3.  $\text{MnO}_4^{-2} + \text{MnO}_2 \longrightarrow \text{MnO}_2 \cdot \text{MnO}_4^{-2}$
4.  $\text{MnO}_2 \cdot \text{MnO}_4^{-2} + 2 \text{H}^+ \longrightarrow \text{MnO}_4^- + \text{Mn(III)} (\text{ppt.})$
5.  $2 \text{Mn(III)} + \text{MnO}_4^{-2} \longrightarrow 3 \text{MnO}_2$
6.  $\text{MnO}_2 (\text{active}) \longrightarrow \text{MnO}_2 (\text{inactive})$

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Figure 5-9. Proposed mechanism for the autodecomposition of neutral permanganate [48].

## CHAPTER 6

### CONCLUSIONS AND FUTURE WORK

By the variation of the molecular geometry of the smallest cluster size for manganese monoxide, namely  $(\text{MnO})_2$ , it is possible to construct a VBDOS curve from the eigenvectors and eigenvalues of the CNDO2/U algorithm which shows remarkable similarity to the spectrum of a thick continuous film of MnO. The significance of this is that it shows that there is another component to XPS valence band broadening which has here-to-fore been overlooked. In past investigations valence band broadening was considered to be due solely from an increase in the size of number of atoms in a cluster on a substrate. In these past investigations the calculated VBDOS curve was broadened by increasing the number of atoms within a given molecular geometry. The geometry most frequently used was face centered cubic (fcc). No consideration was given to the interface between the carbon foil and the dispersed material. In consideration of the interface it is assumed that the substrate contains "sites" which will accommodate certain geometries over others. If certain geometries are accommodated over others it stands to reason that some are going to be less energetically favorable than others. If less energetically favorable geometries are contributing to the photoelectron spectrum, then there is going to

be a broadening in that spectrum. The greater the number of geometries present on the surface of the substrate, the greater the number of molecular orbital energies (i.e. eigenvalues) which are going to contribute to the XPS spectrum. The overall effect of considering the interface between the substrate and the dispersed material is that it demonstrates a limitation in the methodology previously used to interpret XPS valence band broadening.

When the method of deposition of a transition metal oxide onto the carbon substrate is varied there is a variation in the results of the quantitative analysis and in the electronic structure of the surface. When vapor deposition is used to disperse the oxide, samples are obtained whose particles were confined to the surface region. It is even possible to construct a continuous film of MnO on the surface of the carbon substrate by this method. When solution deposition is used to disperse the oxide, the samples obtained have the majority of their dispersed particles incorporated below the surface of the substrate. The electronic structure of the particles dispersed by these two methods is determined by acquisition of data in the valence band region. Particles deposited by the vapor deposition method show a greater valence band narrowing and a greater shift in binding energy away from the Fermi level relative to their bulk oxide than do particles deposited by solution deposition. Thus, vapor deposition seems to cause smaller particles to be deposited on the surface than does solution deposition.

When the dispersed Mn oxide samples produced by both methods are placed into a solution of potassium permanganate, they have an effect on the autocatalytic decomposition of permanganate. It is

shown that the dispersed  $\text{MnO}_2$  has the greatest effect on the decomposition. This would be expected since the  $\text{MnO}_2$  catalyzes the reaction. However the effect of dispersed  $\text{MnO}_2$  may be overestimated. The reason for this may be because the particles incorporated below the surface are contributing to the decomposition. These particles are not considered in the coverage value. The dispersed  $\text{MnO}$  has the second greatest and then the dispersed  $\text{Mn(III)}$  oxide has the third greatest effect. The continuous film and bulk of the  $\text{Mn(III)}$  oxide had the least effect. An explanation as to how the  $\text{MnO}$  affects the reaction is not clear at this point. An explanation is given for why the  $\text{Mn(III)}$  oxide affects the reaction however. Its presence may allow the bypassing of several steps in a mechanism proposed by Duke [48]. The bypassing of these steps would eliminate the need for hydrogen ion, which is very low in a neutral solution.

Future work in the area should center on investigating the effect, if any, of the incorporation of the manganese dioxide particles into the carbon substrate upon the autocatalytic decomposition of permanganate. At present there is experimentation underway which is involved with the deposition of  $\text{MnO}_2$  on mica and glass. Mica is a layered and glass is an unlayered substrate. Knowing the effect of these samples upon the autocatalytic decomposition would enable conclusions to be drawn as to whether the incorporated manganese dioxide particles are responsible for the rate of the permanganate reaction being too high. Future work should also be focused on the quantification of the catalytic activity of dispersed ferric oxide on

carbon foil. The bulk and dispersed samples could be allowed to catalyze the reaction given by



The monitoring of the catalytic activity could be accomplished by gas chromatography (GC) or by in situ reaction in a gas cell. In the former case, the gases involved along with the ferric oxide sample could be placed into a sealed container and samples could be withdrawn at selected time intervals. GC would tell how much of the gases were present at any one particular time. In the latter case, core level  $\text{C}_{1s}$  and  $\text{O}_{1s}$  XPS spectra can be used to monitor the reaction.

## APPENDIX

### STATISTICAL ANALYSIS OF XPS VALENCE BAND DATA

Because interpretations are being made due to the differences in binding energies and FWHMs of valence band data, it is necessary to perform a statistical analysis of data acquired from this region. To do this, the data of 10 different scans of bulk  $\text{Mn}_2\text{O}_3$  are acquired at a take off angle of 0 degrees between 15 and 0 electron volts. After the scans are acquired, the appropriate windows are constructed and the background is subtracted out. The binding energies and the FWHMs of the distributions are determined and the mean and the standard deviations are computed. Table A-1 lists the results.

Table A-1  
Binding energies and FWHMs of the distributions in the valence band region of bulk  $\text{Mn}_2\text{O}_3$

| Scan | Binding Energy (eV) | FWHM (eV) |
|------|---------------------|-----------|
| 1    | 3.93                | 5.34      |
| 2    | 4.25                | 5.77      |
| 3    | 4.40                | 6.07      |
| 4    | 3.85                | 5.16      |
| 5    | 4.22                | 5.88      |
| 6    | 4.33                | 5.82      |
| 7    | 4.33                | 6.25      |
| 8    | 4.51                | 6.10      |
| 9    | 4.25                | 5.74      |
| 10   | 4.33                | 5.96      |

These values resulted in a mean binding energy of 4.26 eV with a standard deviation of 0.18 eV. The mean FWHM is 5.78 eV with a standard deviation of 0.30 eV.

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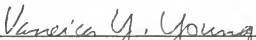
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## BIOGRAPHICAL SKETCH

Jack Davis was born on June 21, 1950, in Kansas City, Missouri. He was raised in nearby Independence where he received his high school diploma in 1968 from William Chrisman High School.

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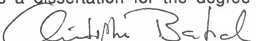
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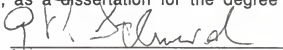
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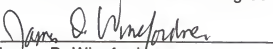
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